Development and functionalization of vegetable oils for plastification and crosslinking of elastomers matrix

Cyrille Betron

N°d'ordre NNT : 2016LYSE054

THESE de DOCTORAT DE L'UNIVERSITE DE LYON
opérée au sein de
l'Université Claude Bernard Lyon 1

Ecole Doctorale ED 34
ECOLE DOCTORALE MATERIAUX DE LYON

Spécialité de doctorat : **Matériaux polymères et composites**
Discipline : Physique-Chimie

Soutenue publiquement le 28/04/2016, par :
Cyrille Bétron

Développement et fonctionnalisation d'huiles végétales pour la plastification et la réticulation d'élastomères

Devant le jury composé de :

Dr.	Pinel Catherine	Université de Lyon 1	Présidente
Pr.	Muller René	Université de Strasbourg	Rapporteur
Pr.	Robin Jean-Jacques	Université de Montpellier	Rapporteur
Dr.	Gregory Martin	Entreprise Hutchinson	Examinateur
Pr.	Cassagnau Philippe	Université de Lyon 1	Directeur de thèse
Dr.	Bounor-Legaré Véronique	Université de Lyon 1	Co-directrice de thèse

UNIVERSITE CLAUDE BERNARD - LYON 1

Président de l'Université	**M. le Professeur Frédéric FLEURY**
Président du Conseil Académique	M. le Professeur Hamda BEN HADID
Vice-président du Conseil d'Administration	M. le Professeur Didier REVEL
Vice-président du Conseil Formation et Vie Universitaire	M. le Professeur Philippe CHEVALIER
Vice-président de la Commission Recherche	M. Fabrice VALLÉE
Directeur Général des Services	M. Alain HELLEU

COMPOSANTES SANTE

Faculté de Médecine Lyon Est – Claude Bernard	Directeur : M. le Professeur J. ETIENNE
Faculté de Médecine et de Maïeutique Lyon Sud – Charles Mérieux	Directeur : Mme la Professeure C. BURILLON
Faculté d'Odontologie	Directeur : M. le Professeur D. BOURGEOIS
Institut des Sciences Pharmaceutiques et Biologiques	Directeur : Mme la Professeure C. VINCIGUERRA
Institut des Sciences et Techniques de la Réadaptation	Directeur : M. le Professeur Y. MATILLON
Département de formation et Centre de Recherche en Biologie Humaine	Directeur : Mme la Professeure A-M. SCHOTT

COMPOSANTES ET DEPARTEMENTS DE SCIENCES ET TECHNOLOGIE

Faculté des Sciences et Technologies	Directeur : M. F. DE MARCHI
Département Biologie	Directeur : M. le Professeur F. THEVENARD
Département Chimie Biochimie	Directeur : Mme C. FELIX
Département GEP	Directeur : M. Hassan HAMMOURI
Département Informatique	Directeur : M. le Professeur S. AKKOUCHE
Département Mathématiques	Directeur : M. le Professeur G. TOMANOV
Département Mécanique	Directeur : M. le Professeur H. BEN HADID
Département Physique	Directeur : M. le Professeur J-C PLENET
UFR Sciences et Techniques des Activités Physiques et Sportives	Directeur : M. Y.VANPOULLE
Observatoire des Sciences de l'Univers de Lyon	Directeur : M. B. GUIDERDONI
Polytech Lyon	Directeur : M. le Professeur E.PERRIN
Ecole Supérieure de Chimie Physique Electronique	Directeur : M. G. PIGNAULT
Institut Universitaire de Technologie de Lyon 1	Directeur : M. le Professeur C. VITON
Ecole Supérieure du Professorat et de l'Education	Directeur : M. le Professeur A. MOUGNIOTTE
Institut de Science Financière et d'Assurances	Directeur : M. N. LEBOISNE

Remerciements

Ce travail de thèse a été réalisé au sein du laboratoire d'Ingénierie des Matériaux Polymères, UMR 5223 à l'Université de Lyon 1. Je tiens donc à remercier en premier lieu le Professeur Philippe Cassagnau de m'avoir accueilli. Étant également mon directeur de thèse, je tiens à le remercier pour la confiance et la liberté d'action qu'il m'a accordées tout au long de ce projet, sa disponibilité en cas de besoin, sa diplomatie… et évidemment ses encouragements distillés avec sobriétés, le tout, toujours assaisonné d'une petite blague bien sentie.

Mes sincères remerciements vont également à ma co-directrice de thèse, Madame Véronique Bounor-Legaré à qui a eu des sueurs froides en ouvrant sa boite mail pendant ces trois années et dont la gentillesse et la patience non d'égal que son emploi du temps surchargé ! Merci d'avoir toujours été présente et de m'avoir apporté votre expertise tout en me laissant une grande autonomie d'action quitte à essuyer quelques échecs olfactifs !

Je suis reconnaissant envers le Professeur Jean-Jacques Robin et le Professeur René Muller pour leur rôle de rapporteur, et membres du jury de thèse. Je tiens à les remercier pour leurs temps et leurs compétences mises à ma disposition pour juger de ce travail. Je tiens également à remercier le Dr Caterine Pinel d'avoir accepté d'être la présidente du jury.

Les travaux présentés dans ce mémoire sont le fruit de la collaboration entre les laboratoires universitaires IMP@Lyon1 et IRCELYON, les entreprises Hutchinson, Serge Ferrari, Activation et EVEA. Je tiens donc à remercier les gens avec qui j'ai pu travailler durant c'est trois années. Et plus particulièrement, Aurélie Vanille de l'entreprise Hutchinson pour son suivie et son implication tout au long de mes travaux de thèse, ainsi que Natacha Carniol et Gregory Martin mes responsables au sein de Hutchinson. Gabriel Scalabrino du laboratoire IRCELYON pour la synthèse et modification des huiles végétales. Valérie Courault pour son accueil et les travaux effectués au sein de l'entreprise Serge Ferrari.

Ma gratitude s'adresse également aux différents financeurs du projet HUMEVERE. Merci pour leur soutien et leur confiance.

Concernant l'aspect technique je tiens à remercier Flavien Mélis pour sa bonne humeur et son expertise précieuse concernant le HAAK, la presse, le rhéomètre et ses pannes d'azotes…

Je voudrai également remercier Adrien Tauleigne dans le domaine de la mise en œuvre d'éprouvettes de tractions et d'échantillons de rhéologies, ainsi que Pierre Alcouffe pour son expertise dans le domaine de la microscopie et sa disponibilité. Je voudrai également exprimer ma gratitude au service RMN du liquide en la personne de Patrick Goetincket Fernande Boisson pour leur aide à la compréhension des spectres RMN des systèmes complexes.

Je voudrai également adresser de profonds remerciements à mes amis rencontrés durant ces trois années et plus particulièrement Charlène Forest, Amélie Chambet et Jihane Sayoune sans qui vous ne liriez certainement pas ces lignes !! Merci à vous pour votre patience et d'avoir supporté mes caprices et états d'âmes sans trop râler, d'avoir pris de votre temps pour être là pour moi tout simplement. Je voudrai également remercier les gens de mon bureau Gauthier, Alice, Loic et Hend qui m'ont entendu râler toute la journée et ont dû subir mes frasques sans jamais me jeter de pierres.

Je remercie également l'ensemble du personnel du laboratoire pour tous les bons moments, entrecoupé d'échanges parfois musclés : Sabine, Sylvie, Nadia, Olivier… Durant ces années à l'IMP, j'ai eu la chance de faire énormément de rencontres avec des gens intéressants, des cultures variées et qui ont su enrichir ma vision des choses : Imed, Jingping, Gauthier, Margarita, Mélanie, Nico, Fabien, Antoine, Sylvain, Pierre, Christoph, Guillaume… Et tous les stagiaires, et les gens qui ne sont passés que brièvement dans ma vie, mais qui ont pourtant contribué à rendre ces années mémorables.

Finalement, j'aimerai remercier ma famille et mes parents qui me supportent depuis ma venue au monde. Qui se demande depuis toutes ces années si faire des mixtures et autres décoctions toute plus infâmes les unes que les autres depuis ma plus tendre enfance dans le jardin me mènerait un jour à autre chose que désherbeur professionnel ! J'espère aujourd'hui leur donner une réponse satisfaisante. Merci à tous mes amis que j'ai rencontrés durant ces longues études, Aude, Morgane, Élodie, Florian, Marc, Marion… et j'en oublie forcément. Enfin merci à Gaya ma petite furette qui me suit partout depuis maintenant 6 ans et qui est toujours là sans jamais dire un mot, mais dont la simple présence ou les catastrophes qu'elle provoque suffisent à me changer les idées.

Et à vous lecteur, puissiez-vous moins galérer à lire cette thèse que moi à l'écrire.

« Être conscient de son ignorance, c'est tendre vers la connaissance. »

Benjamin Disraeli

« La théorie, c'est quand on sait tout et que rien ne fonctionne. La pratique, c'est quand tout fonctionne et que personne ne sait pourquoi. Ici, nous avons réuni théorie et pratique : Rien ne fonctionne... et personne ne sait pourquoi ! »

Albert Einstein

À tous les gens

que je porte dans mon cœur

Table des matières

Publication 4: “EPDM crosslinking from bio-based vegetable oil and alkoxysilane hydrolysis-condensation reactions”

Introduction générale

I- Contexte du projet

La hausse importante du coût des matières premières à base de ressources fossiles ayant eu lieu entre 2007 et 2011 du fait de l'effet conjoint d'une diminution des volumes et d'une demande soutenue en provenance des pays en forte croissance comme les BRIC (Brésil, Russie, Inde et Chine) ont confronté les industriels dans le domaine des polymères à une situation économique difficile.

De plus parallèlement à cette situation économique, les sociétés civiles ont demandé la mise sur le marché de produits ayant des impacts environnementaux et sanitaires limités. L'innovation est donc la clef pour pouvoir répondre aux défis environnementaux et aux pressions économiques internationales de plus en plus fortes. Dans le cadre de ce défi s'est inscrit le projet HUMEVERE en 2011, ayant pour ambition de développer de nouvelles huiles plastifiantes pour formulation PVC et réticulation d'élastomères issus de bio-ressources (huiles végétales).

Cependant, comme le montre la courbe de variation du prix du pétrole (Figure 1) , la situation économique s'est inversée durant 2014 et 2015. Le prix du baril de pétrole ayant été pratiquement divisé par trois entre 2011 et 2015, les ressources fossiles sont devenues à nouveau très compétitives par rapport à des ressources agrosourcées. Malgré cela, la conférence annuelle sur le climat à Paris (COP21) a abouti à un accord « universel et contraignant » montrant ainsi que la volonté politique de limiter l'utilisation de ressources non renouvelables est toujours forte. Les entreprises et les académique doivent donc continuer d'innover pour se préparer le mieux possible à cette transition.

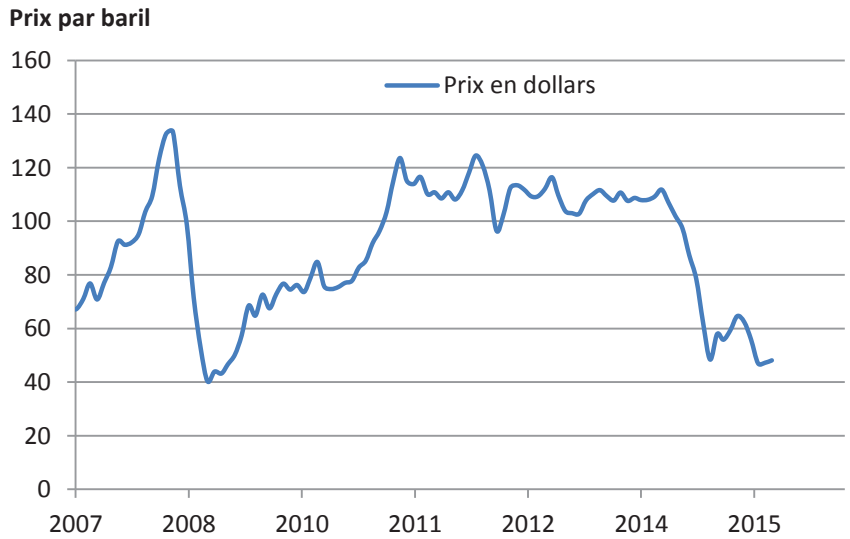


Figure 1: Prix du pétrole (Brent) en dollars[1]

Il est donc important de trouver des alternatives aux huiles plastifiantes, telles que des huiles végétales. Néanmoins, cette substitution ne doit pas être faite au détriment des performances techniques. Les nouveaux produits développés à base d'agroressource devront

rester compétitifs sur le plan technique. Également, la nature biosourcée de ces huiles n'en fait pas une garantie d'un impact sanitaire positif sur les usagers. Elles devront donc être compétitives également en termes de respect de l'environnement.

Les huiles végétales sont composées de triglycérides insaturés. Elles apparaissent comme potentiellement bien adaptées dans l'industrie des polymères, car elles peuvent être utilisées dans différents développements, comme la polymérisation de polymères et la formulation en tant qu'additifs (plastifiants fonctionnels, agents réticulants). Dans le cadre de notre projet, le but est d'utiliser ces huiles comme additifs. De plus ces huiles s'adressant à un marché de plus faible tonnage, ne devront pas venir en concurrence directe avec le secteur de l'agroalimentaire.

L'un des objectifs du projet HUMEVERE est donc de valoriser ces huiles en les fonctionnalisant. Par exemple, la société SERGE FERRARI souhaite profiter du développement de ces nouveaux plastifiants PVC pour conférer à ces nouvelles formulations deux fonctions particulières, à savoir l'ignifugation et une action antifongique. La mise sur le marché de tels produits permettra à la société de supprimer non seulement l'utilisation des plastifiants actuels comme les phtalates, interdits pour certaines applications, mais également l'ajout de charge de type trioxyde d'antimoine pour l'ignifugation. Quant à la société HUTCHINSON, elle souhaite remplacer une partie des plastifiants fossiles utilisés dans les matériaux TPV pour utiliser ces huiles fonctionnelles comme agent de réticulation afin de substituer les peroxydes organiques. La substitution des huiles fossiles par des huiles végétales représente un enjeu important autant pour des raisons environnementales que pour des raisons économiques en cas de nouvelles hausses du prix des matières premières. Les volumes impactés étant de l'ordre de plusieurs milliers de tonnes.

Dans cette optique de remplacement des huiles issues des ressources fossiles par des huiles agrosourcées un consortium d'entreprise a été construit dans le cadre du FUI HUMEVERE. Ce projet a débuté en octobre 2012 en collaboration avec les sociétés HUTCHINSON, SERGE FERRARI, NOVANCE, EVEA et les laboratoires de recherche académique IRCELYON et IMP.

II- Formulations biosourcées : État de l'art

L'application des huiles biosourcées dans le domaine des matériaux polymères a suscité de nouveaux programmes de recherche. Par exemple en 2004, le département américain de l'Énergie a lancé un programme de recherche sur la biomasse afin de l'utiliser en tant que synthons dans le cadre de la synthèse de polymères. À noter que le ministère américain de l'Énergie a établi en 2004 la liste des synthons élémentaires qui peuvent être des alternatives aux monomères conventionnels en vue de la production de polymères destinés à certaines applications. Ce rapport a mis en évidence la potentialité de deux groupes principaux: les dérivés de sucre et les huiles végétales fonctionnalisées. En ce qui concerne les dérivés de sucre, ce rapport identifie douze synthons qui peuvent être produits à partir de sucres par le biais de conversions biologiques ou chimiques. Ces douze synthons peuvent être ensuite transformés en un certain nombre de matériaux à haute valeur ajoutée. Dans la même optique, nous pouvons citer le travail de Bocqué et al. [2] qui donne un aperçu des études

effectuées ces dernières années sur le domaine des plastifiants et plus particulières sur des plastifiants issues de la biomasse. Cette étude montre que les travaux ne se limitent pas exclusivement aux huiles végétales et huiles modifiées, mais que des produits tels que le glycérol, le cardanol, l'alcool de sucre, l'isosorbide d'ester et l'acide citrique ont été étudiés en tant que plastifiant. Les dérivés du sucre sont obtenus par réaction d'hydrolyse de l'amidon et de la cellulose, puis par ouverture de cycles, ces étapes permettent d'obtenir par exemple du xylitol, du sorbitol, de l'isosorbide, etc. L'alcool de sucre possède des propriétés similaires au glycérol et est principalement utilisé pour la plastification de l'amidon. L'isosorbide et ses dérivés sont quant à eux utilisés pour la plastification du PVC.

Aux États-Unis, on trouve également des recherches sur la valorisation de la biomasse visant à développer des systèmes catalytiques pour des chimies telles que l'hydroformylation pour fonctionnaliser les huiles végétales et les convertir en polyols, polyacides, et polyamines [3].

En effet, la présence d'une quantité plus ou moins importante de double liaison sur les huiles végétales leurs permettent d'être utilisées comme sites participant au durcissement de revêtements [4]. Elles peuvent également être modifiées pour obtenir des matériaux polymères à haute performance via l'introduction de groupes réactifs tels que les groupes hydroxyle, époxyde, amine ou carboxyle [5, 6]. D'autre part, l'époxydation, qui est la réaction la plus importante de la fonctionnalisation de ces doubles liaisons C=C, peut être obtenue par des procédés respectueux de l'environnement tels que l'oxydation catalytique par du peroxyde d'hydrogène ou par oxydation enzymatique comme montré sur la Figure 2. Ce type d'huile modifiée est actuellement produit à l'échelle industrielle.

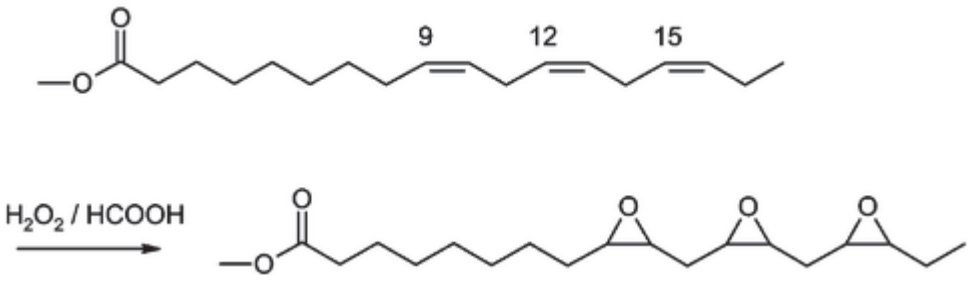


Figure 2: Exemple d'époxidation de méthyle linolénate avec du peroxyde d'hydrogène par procédé catalytique d'acide performique [6].

Il est intéressant de noter que les huiles végétales époxydées partagent de nombreuses caractéristiques des thermodurcissables conventionnels à base d'époxyde. Ainsi, les huiles naturelles de type époxyde, (huiles végétales obtenues principalement à partir de soja, mais aussi de lin ou de ricin) ont été polymérisées [7] à partir de durcisseurs classiques comme les diamines ou dianhydrides [8-11]. On peut citer par exemple l'équipe IAM de Montpellier [12] qui a mis au point la première formulation de résine époxyde dont la résine et le durcisseur sont issus d'huiles modifiées. D'autre part, plusieurs méthodologies ont été développées avec succès pour la synthèse de polyuréthane vert à partir d'huiles végétales fonctionnalisées hydroxylées. L'huile de soja est l'huile généralement la plus utilisée pour la préparation de tels polyols. Au niveau français, l'ITERG (Institut des Corps Gras) et le Laboratoire de Chimie

des Polymères Organiques (LCPO UMR CNRS-Université de Bordeaux) ont déposé récemment plusieurs brevets et publiés des travaux concernant la synthèse de polymère à partir d'huiles animales et végétales (voir Cramail et al.[13-15]). Il y a aussi un certain nombre de recherches concernant la synthèse d'élastomères à partir d'huiles végétales époxydées. Par exemple le travail de Boonkerd et al. [16, 17] qui utilisent la polymérisation anionique de l'huile de soja époxydé pour développer un élastomère fonctionnalisé. Les résultats obtenus lors de ces travaux montrent de bonnes propriétés mécaniques, ce qui est très encourageant pour l'élaboration de ce type de polymères.

Une autre voie chimique envisagée est la modification des huiles et des graisses naturelles par la métathèse. Par exemple, l'homométathèse conduit à la synthèse de longues chaînes alcènes et diesters, molécules qui pourraient trouver des applications dans les polyoléfines, polyamides ou polyesters (Figure 3).

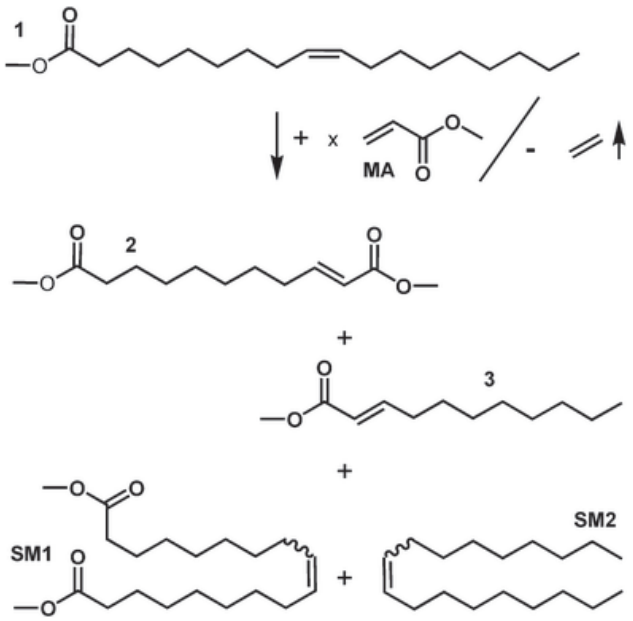


Figure 3: Métathèse croisée de l'oléate de méthyle (1) avec de l'acrylate de méthyle (obtention de deux produits secondaires SM1 et SM2 issus de l'homométhathèse) [18]

Par ailleurs, la métathèse croisée permet la formation de diesters qui pourraient être utilisés dans des applications polymères [18-21]. Néanmoins, la plupart de ces voies de synthèse utilisent des complexes organo-métalliques coûteux à base de ruthénium.

Une autre application potentielle des huiles végétales est en tant qu'additif plastifiant de matériaux polymères. À l'heure actuelle, les recherches sont particulièrement concentrées sur le remplacement des phtalates dans le PVC, et à ce titre on trouve de nombreux articles de recherches et brevets industriels. Les premiers brevets datent du début des années 2000 [22], mais depuis, d'autres brevets ont été régulièrement publiés pour répondre à cette problématique [22-27]. Plus récemment les partenaires IMP et IRCELYON ont étudié, en collaboration avec la société SERGE FERRARl dans le cadre d'un projet AGRICE de l'ADEME [28], la modification d'huiles végétales pour la synthèse de nouveaux plastifiants PVC. Ainsi des bioplastifiants du PVC ont été préparés en trois étapes catalytiques. Après

transestérification des huiles par des alcools, les esters gras ont été époxydés puis l'époxyde résultant a été ouvert avec un anhydride en présence de quantité catalytique de sels d'ammonium. Une large gamme de produits a été préparée à partir de différentes sources d'huiles végétales. Selon l'origine de l'huile, il a été constaté que les propriétés physico-chimiques du plastisol (suspension de grains de PVC dans le plastifiant) sont dépendantes du nombre moyen d'insaturations du triglycéride. Les meilleures propriétés (pouvoir plastifiant) ont été obtenues à partir de l'ester oléate méthylique Figure 4 [29, 30]. Ces huiles plastifiantes sont en cours de développement à l'échelle de la tonne par la société FERRARl. Ces résultats sont très encourageants, toutefois de nouvelles fonctionnalités sont demandées à ces huiles, principalement dans le cadre de la tenue au feu des matériaux (propriétés ignifugeantes).

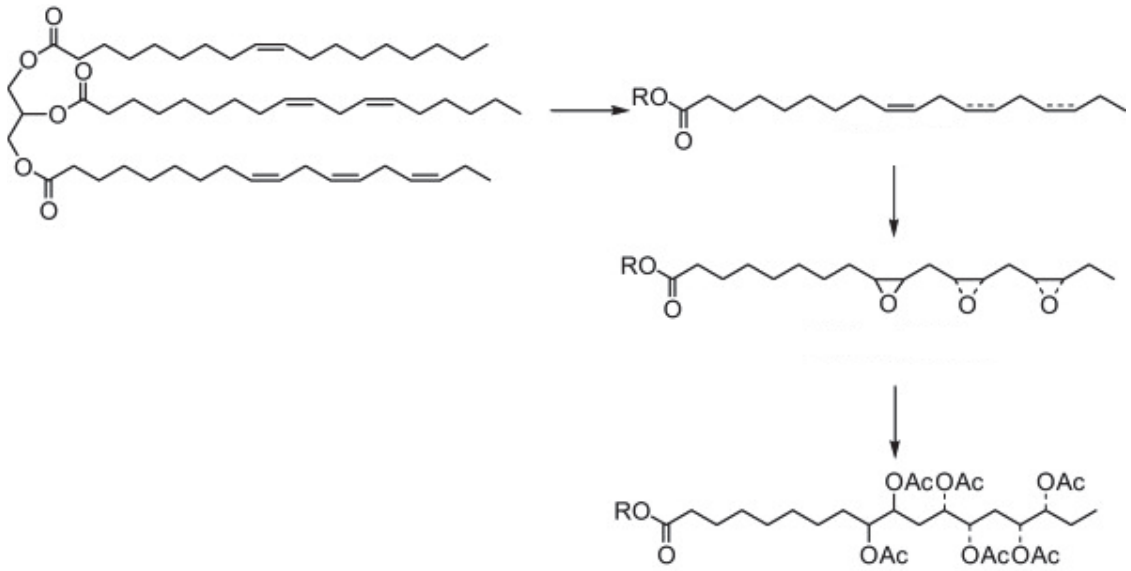


Figure 4 : Exemple de schéma de synthèse permettant de fonctionnaliser une huile végétale pour l'utiliser comme plastifiant PVC [30]

Différentes molécules issues de matières premières végétales sont évaluées comme bioplastifiant du PVC. On peut notamment citer les dérivés de l'huile de ricin commercialisé par la société DANISCO sous le nom GRINDSTED SOFT-N-SAFE® pour des applications telles que l'emballage alimentaire, industrie des équipements médicaux, etc. Le plastifiant à base d'huile de ricin a été testé par SERGE FERARRI avec leur formulation spécifique, mais il n'a pas passé le test visant à déterminer la migration des plastifiants au cours du temps à la surface d'un échantillon. Les dérivés diesters de pisosorbide, développés par la société ROQUETTE ont aussi des applications potentielles comme bioplastifiants. La recherche de bioplastifiant du PVC est toujours d'actualité comme le montrent les brevets de 2012-2014 concernant la plastification de PVC par des huiles végétales [31-33]. Comme candidat à la substitution des phtalates dans les PVC, on peut également citer le cardanol obtenue par distillation des coquilles de noix de cajou. Les premiers travaux datent de 1976 avec Neuse et al. [34, 35] qui mettent en avant les performances prometteuses de ce plastifiant. Il faudra ensuite attendre 2010 pour que de nouvelles études s'intéressent de nouveau à ce composé avec les travaux de Greco et al. [36] et Calo et al. [37]. Si ces études montrent une bonne miscibilité du plastifiant avec la matrice PVC, son efficacité limitée le cantonne à une

utilisation en tant que plastifiant secondaire. Ces recherches montrent que diverses solutions ont été étudiées et développées. Néanmoins ces formulations ne sont pas encore complètement satisfaisantes et elles nécessitent donc encore des travaux de recherche pour pouvoir substituer complètement les phtalates de manière satisfaisante par des molécules agro-sourcées.

Les travaux concernant la plastification des élastomères par des huiles végétales sont quant à eux beaucoup moins nombreux. En effet, il faut noter que naturellement les matrices élastomères sont peu compatibles avec les huiles végétales du fait de leur polarité. Par exemple, des essais de compatibilité entre une matrice élastomère et du biodiesel issue de l'huile de palme [38] ont donné des résultats peu probants en raison de la présence d'esters. Néanmoins, on peut tout de même citer d'autres articles récents comme celui de Petrovic et al. [39] concernant la plastification de TPV à base de caoutchouc naturel par de l'huile de soja. Également, Wang et al. [40, 41] ont étudié les différences de propriétés pour des matrices EPDM et NBR plastifiées avec des huiles pétrosourcées et par de l'huile de soja. Ces dernières études donnent des résultats bien plus satisfaisants avec des propriétés mécaniques proches de celles obtenues avec des plastifiants classiques issus des ressources fossiles.

Enfin, il faut remarquer que les polyols biosourcés ne peuvent pas encore totalement rivaliser avec leurs homologues d'origine fossile en termes de performances et de coût. Même si les avancées dans ce domaine sont importantes, leurs propriétés physico-chimiques restent encore limitées, notamment en raison des longueurs de chaînes mal adaptées, mais également de leur pureté souvent insuffisante. En effet, les huiles végétales n'étant pas des composés purs, mais des mélanges statistiques d'acides gras, la fonctionnalisation est souvent aléatoire et engendre une limitation rédhibitoire dans le contrôle de l'architecture moléculaire, principalement pour la synthèse de polymères thermoplastiques. De plus, si l'on considère que la composition varie d'une huile à l'autre, mais également d'une saison et d'une région à une autre, on se rend compte de la difficulté que représente la fonctionnalisation et la gestion de l'architecture moléculaire de tels produits. Mais heureusement la maîtrise de cette fonctionnalité n'est pas un paramètre critique pour l'application d'huiles fonctionnelles dans des applications en tant que plastifiants (PVC, élastomères) ou de réactifs (agent de réticulation) qui nous intéressent dans ce travail de thèse.

Toutes ces études montrent que la substitution des huiles issues des ressources fossiles par des huiles agrosourcées est une problématique actuelle. De plus, les travaux effectués montrent le potentiel des huiles végétales comparé à des huiles issues des ressources fossiles. Les résultats mécaniques obtenus dernièrement avec des huiles biosourcées sont encourageants et montrent le potentiel des huiles végétales pour remplacer à terme les huiles minérales classiques.

III- Organisation des travaux

Pour atteindre les résultats escomptés, qui sont le remplacement des plastifiants actuels par des huiles végétales et le développement des nouvelles méthodes de réticulation, nous avons organisé notre travail de la façon suivante :

Dans le premier chapitre de cette étude, nous avons concentré nos recherches sur la potentialité de différentes molécules pouvant répondre au cahier des charges fourni par les sociétés HUTCHINSON et SERGE FERRARI pour les matrices EPDM et PVC respectivement. Des modèles théoriques, basés sur les paramètres de solubilité de Hansen, ont été étudiés pour déterminer une architecture et une géométrie moléculaire viable des huiles que nous tenterons de synthétiser par la suite. Ces analyses théoriques seront ensuite mises en parallèle à des expériences de diffusion par analyse rhéologique. La comparaison de ces résultats permettra de tester les limites du modèle théorique déjà connu et régulièrement utilisé. De plus, ces études permettront de sélectionner les molécules de forts potentiels.

Dans la suite du projet, nous nous sommes focalisés principalement sur les huiles pour matrice élastomère. Les huiles pour PVC, ont été étudiées plus en détails par le laboratoire IRCELYON.

Basée sur cette étude préalable, dans le chapitre 2 nous étudierons un certain nombre d'huiles issues de bioressources et nous vérifierons qu'elles sont des bons plastifiants pour un élastomère. Nous mettrons également en œuvre une technique permettant de résoudre les problèmes de compatibilités rencontrés lors de la plastification d'une matrice élastomère par une huile végétale. Cette méthode suit les règles de la chimie verte et donc l'aspect environnemental du projet, en limitant au maximum les étapes de synthèses et l'utilisation de réactifs.

Dans le chapitre 3, une fonctionnalité telle que celle d'agent de réticulation sera étudiée afin d'apporter une plus-value supplémentaire à l'utilisation d'additifs issus d'agroressources. Dans cette partie, nous mettrons en évidence une méthode de plastification et de réticulation sans utilisation de catalyseur.

Enfin dans le chapitre 4, nous présenterons une méthode de réticulation toujours basée sur l'utilisation d'une huile végétale, mais avec la création d'un réseau siloxane par réaction hydrolyse-condensations de la fonction alkoxysilane.

IV- Bibliographie

1. INSEE. *Cours des matières premières importées - Pétrole brut "Brent" (Londres) - Prix en euros par baril*. 2015 [cited 2015; Available from: http://www.insee.fr/fr/bases-de-donnees/bsweb/serie.asp?idbank=001565198.
2. Bocqué, M., et al., *Petro-based and bio-based plasticizers: Chemical structures to plasticizing properties.* Journal of Polymer Science Part A: Polymer Chemistry, 2016. **54**(1): p. 11-33.
3. Kandanarachchi, P., A. Guo, and Z. Petrovic, *The hydroformylation of vegetable oils and model compounds by ligand modified rhodium catalysis.* Journal of Molecular Catalysis A: Chemical, 2002. **184**(1–2): p. 65-71.
4. Sharmin, E., et al., *Recent advances in vegetable oils based environment friendly coatings: A review.* Industrial Crops and Products, 2015. **76**: p. 215-229.
5. Seniha Güner, F., Y. Yağcı, and A. Tuncer Erciyes, *Polymers from triglyceride oils.* Progress in Polymer Science, 2006. **31**(7): p. 633-670.
6. Meier, M.A.R., J.O. Metzger, and U.S. Schubert, *Plant oil renewable resources as green alternatives in polymer science.* Chemical Society Reviews, 2007. **36**(11): p. 1788-1802.
7. Park, S.-J., F.-L. Jin, and J.-R. Lee, *Effect of Biodegradable Epoxidized Castor Oil on Physicochemical and Mechanical Properties of Epoxy Resins.* Macromolecular Chemistry and Physics, 2004. **205**(15): p. 2048-2054.
8. Miyagawa, H., et al., *Thermo-Physical and Impact Properties of Epoxy Containing Epoxidized Linseed Oil, 2.* Macromolecular Materials and Engineering, 2004. **289**(7): p. 636-641.
9. Miyagawa, H., et al., *Fracture toughness and impact strength of anhydride-cured biobased epoxy.* Polymer Engineering & Science, 2005. **45**(4): p. 487-495.
10. Earls, J.D., et al., *Amine-cured ω-epoxy fatty acid triglycerides: Fundamental structure–property relationships.* Polymer, 2007. **48**(3): p. 712-719.
11. Ahmad, S., et al., *Development of amine–acid cured Annona squamosa oil epoxy anticorrosive polymeric coatings.* Progress in Organic Coatings, 2006. **55**(3): p. 268-275.
12. Stemmelen, M., et al., *A fully biobased epoxy resin from vegetable oils: From the synthesis of the precursors by thiol-ene reaction to the study of the final material.* Journal of Polymer Science Part A: Polymer Chemistry, 2011. **49**(11): p. 2434-2444.
13. Cramail, H., et al., *Nouveaux dérivés d'huile de ricin et leur procédé de préparation*, 2012, Patent.
14. Cramail, H., et al., *Nouveau procédé de préparation de polyols et produits tels qu'obtenus*, 2011, Patent.
15. Cramail, H., et al., *Précurseurs biscarbonates, leur procédé de préparation et leurs utilisations*, 2011, Patent.
16. Boonkerd, K., et al., *Formation of a novel bio-based elastomer from polybutadiene and epoxidized soybean oil via post-living anionic polymerization.* Journal of Elastomers and Plastics, 2014. **46**(7): p. 644-661.
17. Zhang, J., et al., *Formation of bio-based elastomer from styrene-butadiene copolymer and epoxidized soybean oil.* Journal of Polymer Research, 2014. **21**(4): p. 1-11.
18. Rybak, A. and M.A.R. Meier, *Cross-metathesis of fatty acid derivatives with methyl acrylate: renewable raw materials for the chemical industry.* Green Chemistry, 2007. **9**(12): p. 1356-1361.
19. Mol, J.C., *Catalytic Metathesis of Unsaturated Fatty Acid Esters and Oils.* Topics in Catalysis, 2004. **27**(1-4): p. 97-104.

20. Jacobs, T., A. Rybak, and M.A.R. Meier, *Cross-metathesis reactions of allyl chloride with fatty acid methyl esters: Efficient synthesis of α,ω-difunctional chemical intermediates from renewable raw materials.* Applied Catalysis A: General, 2009. **353**(1): p. 32-35.
21. Riepl, H.M., et al., *Self Metathesis of Fatty Alcohols and Amines to Provide Monomers for Polyester and Polyamide Products.* Macromolecular Symposia, 2010. **293**(1): p. 39-42.
22. Benecke, H.P., J.D. Elhard, and B.R. Vijayendran, *Plasticizers derived from vegetable oils*, 2000, Patent.
23. Hinault, R., C.H. Le, and J. Barbier, *Esterified fatty acids for the plasticizing of pvc*, 2006, Patent.
24. Parker, H.W., et al., *Castor Oil/Epoxidized soybean oil based elastomeric compositions*, 2009, Patent.
25. Ruschel, R.C.B. and J.G. Martins, *Vegetal oil derivatives plasticizers*, 2009, Patent.
26. Eaton, R., *A replacement plasticizer system for phthalate-plasticized formulations*, 2009, Patent.
27. Augusto, C.J. and D.Q.J.J. Vianna, *Primary PVC plasticizers derived from vegetable oils, process for obtaining primary PVC plasticizers derived from vegetable oils and plasticized PVC composition*, 2009, Patent.
28. Pinel, C., et al., *Biodegradable plasticizers for polymers*, 2011.
29. Rouzeau, S., et al., *Method for preparing polymer bioplasticizers*, 2009, Patent.
30. Fogassy, G., et al., *Catalyzed ring opening of epoxides: Application to bioplasticizers synthesis.* Applied Catalysis A: General, 2011. **393**(1–2): p. 1-8.
31. Kodali, D.R., L.J. Stolp, and M. Bhattacharya, *Bio-renewable plasticizers derived from vegetable oil*, 2013, Patent.
32. Ghosh-dastidar, A., et al., *Vegetable-oil derived plasticizer*, 2012, Patent.
33. De Quadros, J.V. and J.A. De Carvalho, *Primary pvc plasticizers derived from vegetable oils, process for obtaining primary pvc plasticizers derived from vegetable oils and plasticized pvc composition*, 2014, Patent.
34. Neuse, E. and J.D. Vanschalkwyk, *Cardanol derivatives as pvc plasticizers .1. synthesis.* South African Journal of Science, 1976. **72**(8): p. 233-237.
35. Neuse, E.W. and J.D. Vanschalkwyk, *Cardanol derivatives as pvc plasticizers .2. plasticizer evaluation.* Journal of Applied Polymer Science, 1977. **21**(11): p. 3023-3033.
36. Greco, A., et al., *Plasticizer for poly(vinyl chloride) from cardanol as a renewable resource material.* Polymer Degradation and Stability, 2010. **95**(11): p. 2169-2174.
37. Calo, E., A. Greco, and A. Maffezzoli, *Effects of diffusion of a naturally-derived plasticizer from soft PVC.* Polymer Degradation and Stability, 2011. **96**(5): p. 784-789.
38. Haseeb, A.S.M.A., et al., *Compatibility of elastomers in palm biodiesel.* Renewable Energy, 2010. **35**(10): p. 2356-2361.
39. Petrovic, Z.S., et al., *Soybean oil plasticizers as replacement of petroleum oil in rubber.* Rubber Chemistry and Technology, 2013. **86**(2): p. 233-249.
40. Wang, Z., et al., *Plasticization Effect of Transgenic Soybean Oil. I. On Ethylene Propylene Diene Monomer (EPDM), as Substitute for Paraffin Oil.* Journal of Applied Polymer Science, 2013. **130**(6): p. 4457-4463.
41. Wang, Z., et al., *Plasticization Effect of Hydrogenated Transgenic Soybean Oil on Nitrile-Butadiene Rubber.* Journal of Applied Polymer Science, 2014. **131**(16).

CHAPITRE I:

Publication 1: “Diffusion of modified vegetables oils in thermoplastic polymers”

Diffusion of modified vegetables oils in thermoplastic polymers

Cyrille Bétron[a], Véronique Bounor-Legaré[a], Catherine Pinel[b], Gabrielle Scalabrino[b], Laurent Djakovitch[b], Philippe Cassagnau[a]

[a] Univ Lyon, CNRS- UMR 5223, Université Lyon 1, Ingénierie des Matériaux Polymères15 Boulevard Latarjet, F-69622 Lyon, France

[b] CNRS, UMR5256, Institut de Recherche sur la Catalyse et l'Environnement de Lyon, IRCELYON, Université Lyon 1, 2 avenue Albert Einstein, F-69626 Villeurbanne, France

Keywords: Polymers, vegetable oils, Hansen solubility parameters, diffusion

Abstract

This paper focused on the study of the diffusion of vegetable oils and their derivatives in thermoplastic polymers. All of the synthesised molecules were based on vegetable oils and more particularly on soybean and rapeseed oils. The first aim of this paper was to examine the Hansen solubility parameters in diffusion experiments in order to identify the strengths and weaknesses of this method. The second aim was to design new vegetable oil substrates able to mimic fossil substrates such as mineral oil (Torilis®) used in EPDM and diisononylphthalate (DINP) used in PVC plastisols. The diffusion ability of these vegetable molecules was studied experimentally using rheological methods. Finally, the study showed that the solubility parameters are useful for predicting suitable molecules in terms of chemical modification of raw vegetables oils. However, rheological experiments are necessary to definitively select the most suitable molecules in terms of their viscosity and final properties.

I- Introduction

The use of renewable resources in the preparation of various industrial materials has seen a revival of interest because of environmental concerns. Petroleum based plasticisers are standard compounding ingredients, however epoxidised vegetable oil-based plasticisers have recently been developed as feasible alternatives. The primary role of such substances is to improve the flexibility and processability of polymers by lowering the glass transition temperature (T_g). These substances reduce the stress relaxation, hardness, density, viscosity and electrostatic charge of a polymer, at the same time as increasing the flexibility and resistance to fracture of the polymer chain [1]. The use of plasticisers for plastic product manufacture is not a new practice. Their application in modifying polymer characteristics began in the 1800s. In those early days, manufacturers of celluloid or celluloid lacquers used natural camphor and castor oil for plasticisation purposes, but they were unsatisfactory for many end uses. Later, in 1912, camphor oil substituted with triphenyl phosphate was tested, representing the beginning of the ester plasticisers era. Phthalic acid esters found applications as plasticisers for the first time in 1920 and continue to be the largest class of plasticisers used in the 21st century [2]. Vegetable oils are excellent renewable raw materials for the synthesis of a range of products including polymers. Derived from plants, they are chemically composed of different triacylglycerols, esters of glycerol and fatty acids [3]. Vegetable oils are attractive raw materials for many industrial applications as they are derived from renewable resources, biodegradable, environmental friendly, easily available and can be produced in large quantities at a competitive cost [4]. Determining factors for the applicability of oils are their composition and price [5]. Historically vegetable oils have been used in the production of alkyl resins for air-drying coatings. Ester groups and double bonds are reactive sites that are present in all oils, and in some oils other sites such as hydroxyl or epoxy groups may be available. The content of unsaturated molecules is measured by determining the iodine value. Edible oils have about five dominating fatty acids. Two are saturated — palmitic (C16:0) and stearic (C18:0) acids, and three are unsaturated — oleic (C18:1), linoleic (C18:2), and linolenic (C18:3) acids. The first number designates the number of carbon atoms in the fatty acid and the second indicates the number of double bonds [6]. Nowadays, there is increasing interest in the use of natural-based plasticisers that are characterised by low toxicity and low migration. This group includes epoxidised triglyceride vegetable oils from soybean oil, linseed oil, castor-oil, sunflower oil, and fatty acid esters (FAEs), and together

they constitute one of the most important classes of renewable resources [4, 7]. Unsaturated vegetable oils have been used for many years in the elaboration of polymeric materials [8-12]. More and more studies with the objective of converting biomass into chemical compounds have been performed over the last ten years [13, 14]. However, the incorporation of this bio-component into classical polymer matrices remains a challenging issue. Compatibility between plasticiser and polymer is of crucial importance for effective plasticisation and various parameters can be used to predict compatibility, including polarity, hydrogen bonding, dielectric constant and solubility parameters [15, 16]. Another important factor is solvation, as plasticisers with solubility parameters close to those of the polymer require less energy to fuse or solvate the polymer. In that context, the aim of this study is to understand the different parameters that contribute to improve the diffusion and solubility of vegetable oils. This study was carried out on two widely used polymers, ethylene propylene diene monomer terpolymer (EPDM) and Poly (vinyl chloride) (PVC). Since its introduction on the market in the early 1960s, ethylene propylene diene monomer terpolymer (EPDM) is one of the most important synthetic rubbers. EPDM exhibits excellent heat, ozone, ageing, weathering and chemical resistance and is employed in a variety of technical applications. These include uses in the automotive industry, in building and construction, in sealing and fitting systems and even as modifiers for thermoplastic materials [17]. Paraffin oil is used in the compounding of diene rubbers such as EPDM to improve the processability of the compounds and to impart the desired physico-mechanical properties to their vulcanisates [18]. PVC is one of the most commonly used polymeric materials. Due to the high consumption of this polymer in the flexible form, the critical problem remains the plasticiser: additives can migrate from the plastic to the surrounding media. The problem becomes very serious in the packaging of foodstuffs and pharmaceuticals, explaining why a considerable volume of legislation has been developed in the European Economic Community (EEC), the United States, and elsewhere [19]. Many factors can influence plasticiser migration, for example temperature, compatibility, and the molecular size of the plasticiser [20, 21]. Therefore, the objective of this study is to understand the mechanisms that influence the diffusion of plasticisers based on vegetable oils in two very different matrices, EPDM and PVC. For these two polymers, we calculated the solubility parameters and checked the reliability of the results experimentally. Based on the work of Bocqué *et al.* [22], describing that the solubility parameter is not sufficient to predict the plasticisation efficiency, we attempt to determine the limits of this method.

Solubility Parameters:

The solubility parameter was introduced by Hildebrand and Scott in 1950 [23, 24] and finally defined by Brydson [25]:

$$\delta = \left(\frac{E}{V_m}\right)^{0.5} = \left[\frac{(\Delta H_{vap} - RT)}{V_m}\right]^{0.5} \quad (1)$$

where the evaporation enthalpy ΔHvap was taken as the parameter of the cohesion energy, E, of a material, corresponding to the increase in the internal energy per mole of the material if all the intermolecular forces are eliminated, and the thermal energy RT needed to separate them. The cohesive energy density δ, is the energy required to break all intermolecular physical links in a unit volume of the material (Vm).

Hansen [26, 27] has shown that the solubility parameter (HSP), proposed by Hildebrand and Scott does not take into account the contribution of polar forces and hydrogen bonding. Therefore, a more complex Hansen solubility parameter (HSP) has been proposed:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (2)$$

derived from the contribution of three components of the cohesive energy (E_{coh}):

$$E_{coh} = E_d + E_p + E_h \quad (3)$$

respectively, due to the contributions from dispersion (E_d), polar forces (E_p) and hydrogen bonding (E_h).

It is possible to calculate the solubility parameter components of almost all molecules and polymers by a group contribution method [28, 29]. For this purpose, as explained by Van Krevelen, it is useful to introduce the molar attraction constant simply defined as:

$$\varphi = (E_{coh} V_m)^{0.5} \quad (4)$$

A set of equations has been proposed by Van Krevelen for the calculation of the solubility parameter component using the molar attraction:

$$\delta_d = \frac{(\sum \varphi)}{V_m} \quad (5)$$

$$\delta_p = \frac{(\sum \varphi^2)^{0.5}}{V_m} \quad (6)$$

$$\delta_h = \left[\frac{\sum E_h}{V_m}\right]^{0.5} \quad (7)$$

The total solubility parameter can be calculated as follows:

$$\delta_t = \left(\delta_d^2 + \delta_p^2 + \delta_h^2\right)^{0.5} \quad (8)$$

Generally, HSP is calculated considering all of the molecular groups [30].

One of the issues with Van Krevelen methods is that they often cannot satisfactorily predict complex inter-group interactions. The Van Krevelen method is focused on the contribution of one chemical function but does not take into account functions located in alpha or beta positions and their contribution is not calculated. In this study, we used the calculation method Y-MB developed by Yamamoto. Yamamoto adapted his Neural Network (NN) methodology for fitting the full HSP data set in such a way that inter-group interactions are automatically fitted by the relative strengths of the neural interconnections. For that purpose, an automatic Molecule Breaking (MB) program that creates sub-groups from any molecule has been developed. Finally, a combination of MB and NN results in the best predictive power for HSP. This method is considered to be the most powerful approach for predicting the Hansen solubility parameter [31] and in our present work is available through the software HSPiP (Hansen Solubility Parameters in Practice).

For a single molecule the generic algorithm is used. The fitting method, using the Standard algorithm, creates very large solubility domains at high δ_d values.

For complex molecules (with molar mass greater than 1000 $g.mol^{-1}$) or natural vegetable oils, this calculation method is not adapted. The "HSPiP" software used in this work has a molar mass limitation that prevents the calculation of the HSP for a functionalised vegetable oil. Moreover, these oils are complex mixtures of fatty acid with varied compositions depending of their source. In these conditions, it is more appropriate to analyse the vegetable oils as a whole and incorporate their complexity rather than to perform to a calculation for each constitutive element. Therefore, for these components, we used the chemical method with 58 solvents. To carry out such an analysis, 200 µl of plasticiser is placed into test tubes with 2ml of solvent. The test tubes are placed on a rolling bench for 24 hours. If the sample is dissolved, a value of 1 is given, if the sample is not dissolved a value of 0 is given. Finally, the solubility is plotted in a Hansen space (3-dimensional: δ_d= dispersive contribution/ δ_p= polar contribution/ δ_h= h-bonding contribution) and the solubility domain can be calculated and represented as in Figure 1.

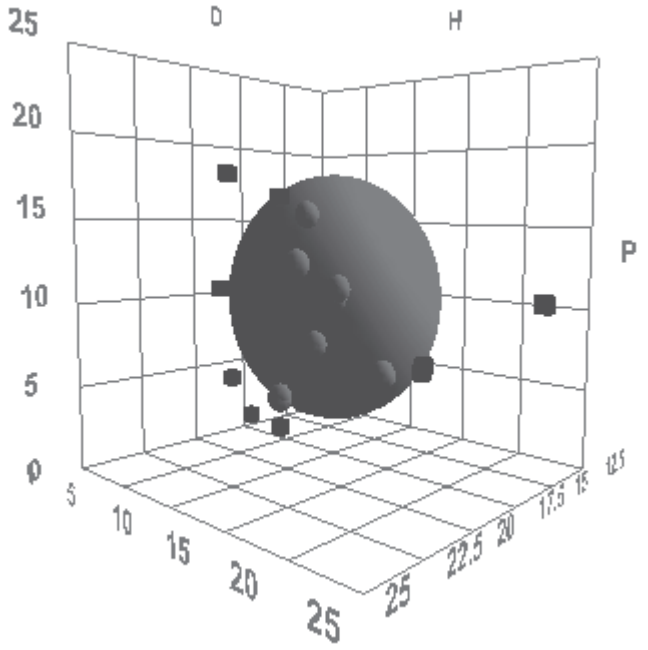


Figure 1. Graphic representation of the polymer matrix interaction. The sphere is the interaction radius of polymer matrix R_0. The dots located inside of sphere (represented by balls), represent a good solvent and the dots located outside the sphere (represented by squares), are characteristics of a bad solvent.

The sphere is the representation in the space of the polymer matrix interaction R_0. If the HSP coordinates of a molecule are located inside this sphere, in theory this molecule is a good solvent. Conversely, if the molecular coordinates are located outside of this sphere, the molecule is considered as a non-solvent. However, the frontier of the sphere is not well-defined and consequently it is more appropriate to consider a solubility gradient from the centre (maximum solubility) to the edges (minimum solubility).

Quantitative evaluation of solubility can be represented using the radius of interactions, R_a $(MPa)^{1/2}$ value, meaning the distance between the HSPs for both solvent (s) and polymer (p) [32, 33].

$$R_a = \left[4({}^s\delta_d - {}^p\delta_d)^2 + \left({}^s\delta_p - {}^p\delta_p\right)^2 + ({}^s\delta_h - {}^p\delta_h)^2\right]^{1/2} \quad (9)$$

In this equation, the *p* terms correspond to the parameters of the polymer and the *s* terms to the parameters of the solvent (or plasticiser). The relative energy difference (RED) is represented using R_0 and R_a $(MPa)^{1/2}$.

$$RED = {}^{R_a}/_{R_0} \quad (10)$$

When RED is $\lesssim$ 1, the solvent is a good solvent, whereas when RED is >1, it is a poor solvent. This can be used as an indicator of solubility [34].

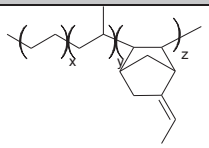
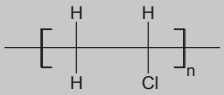
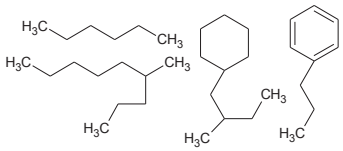
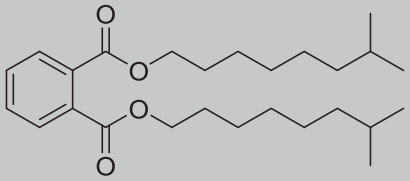
II- Experimental

Polymers:

The EPDM used is Vistalon® 8800 (Exxon Mobil Chemical), a terpolymer that comprises 53.5% wt. ethylene/36.5% wt. propylene/10% wt. ethylidene norbornene. The following values of molar mass were measured: M_n= 170 000 $g.mol^{-1}$ and M_w= 310 000 $g.mol^{-1}$. This terpolymer is oil-extended with 13% wt. mineral oil. These materials were kindly supplied by Hutchinson. The EPDM samples were prepared in an internal batch mixer (Haake Rheomix 50 cm^3), at 160 °C and 50 rpm. The following protocol was adopted: First, the polymer was introduced into the cavity and mixed for 5 min in order to ensure thermal homogeneity. Thereafter, all samples were compression moulded into 1 mm-thick sheets at 180 °C for 10 min and at 130 °C for 5 hours to reduce stress relaxation.

The PVC used is a Lacovyl® PVC (Arkema) produced by a micro-suspension polymerisation process for the preparation of plastisols. In detail, PVC plastisol is a suspension consisting of particles of PVC resin in a continuous liquid phase formed mainly by a plasticiser [35]. In the present study, we studied the plastisol gelation curve for formulations containing 30% wt. of plasticiser. In addition, 2% wt. of thermal stabilizer supplied by SERGE FERRARI was added in the formulation.

Table 1. Chemical structure of polymers and petro-based plasticizers

Entry	Name	Molecule	Molar mass ($g.mol^{-1}$)
1	Vistalon® 8800 EPDM		
2	Lacovyl® PVC		
3	Torilis® 7200 (Mineral oil)		Ø
4	DINP		419

Vegetable oils and their modified derivatives:

The EPDM reference oil is a mineral oil called Torilis® 7200 from Total. The PVC reference oil is the DINP (diisononylphthalate) Jayflex™ from ExxonMobil Chemical, their chemicals structures and their names are resumed in the Table 1. The natural vegetable oils were supplied by Oléon for the linseed oil **8**, soybean oil **6** and epoxidised soybean oil **12** as well as methyl oleate **13**, methyl linoleate **14** and epoxidised methyl ester of soybean oil **15**. The Tung oil **9** and safflower oil **7** were supplied by Sigma-Aldrich (Table 2) and composed of several fatty esters described in Figure 2.

Table 2. Composition of vegetable oils

Entry	Name	Composition (wt%)					Double bond content / Chain	Mw g.mol^{-1}
		C16:0	C18:0	C18:1	C18:2	C18:3		
6	Soybean oil[a] (SBO)	7-11	2-7	20-30	43-50	8-14	1.5	≈900
7	Safflower oil[a]	6-8	3-4	13-20	70-75	1-3	1.7	≈900
8	Linseed oil[a]	4-7	2-5	18-22	13-17	45-60	2.2	≈900
9	Tung oil	C18:0	C18:1	C18:2	α-eleostearic acid (9Z, 11E, 13E)		2.7	≈900
		5.5	4	8.5	82			

[a] *data from Oleon Company.*

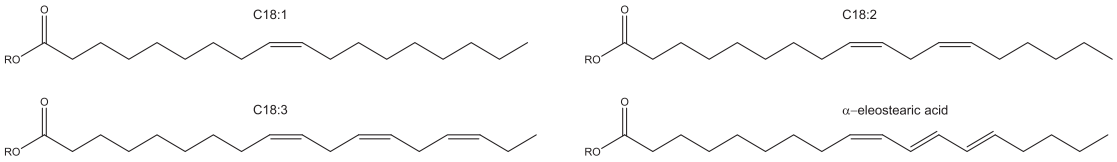
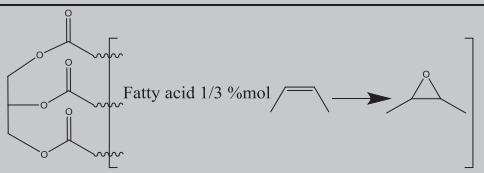
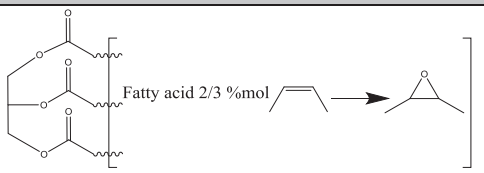
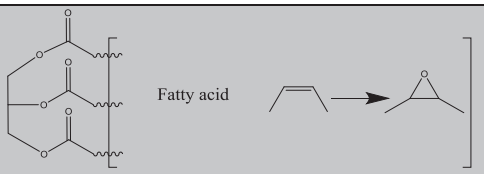
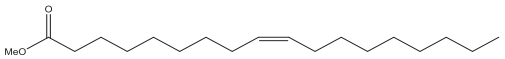
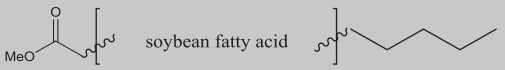
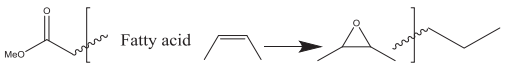
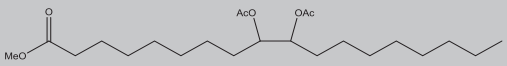
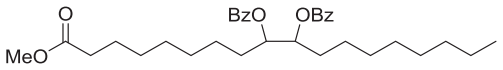
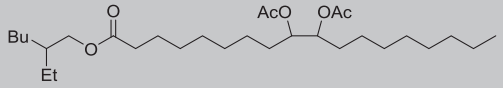
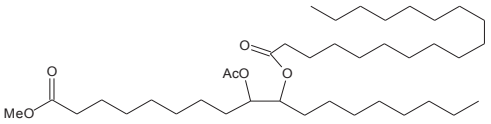
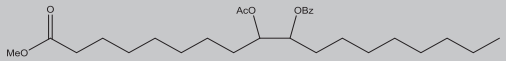
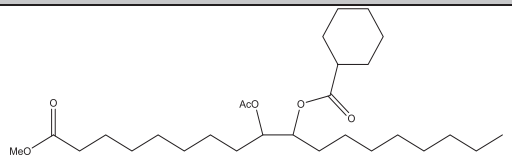
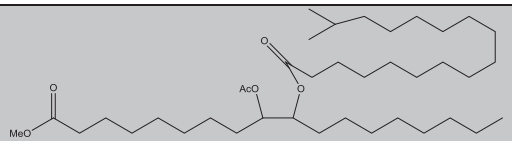
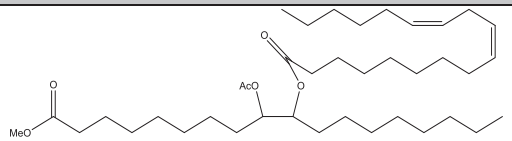
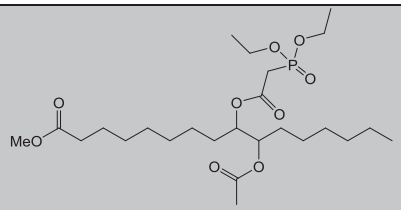
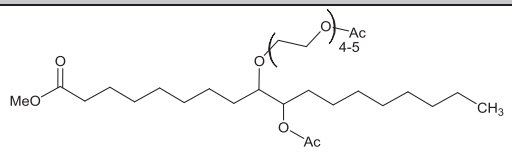
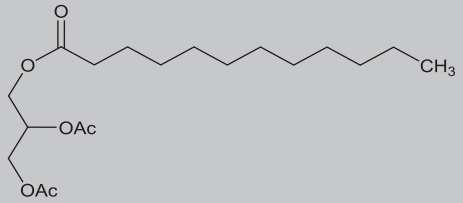


Figure 2. Chemical structure of fatty esters

Table 3. Representative structure of the modified vegetable oils used as bioplasticizers

Entry	Name	Representative molecule	Molar mass ($g.mol^{-1}$)
10	1/3 ESBO Partially Epoxidized soybean oil		901
11	2/3 ESBO Partially Epoxidized soybean oil		917
12	ESBO Epoxidized soybean oil		933
13	MO Methyl oleate (83% purity) FD = 1.1		296
14	MeSBO Methyl ester of soybean oil (65% purity) FD = 1.5		294
15	MeESBO Epoxidized methyl ester of soybean oil FD = 1.4		312
16	DiAc MeSBO FD = 1.4		414

17	DiBz MeSBO FD = 1.4		538
18	DiAc isooctyl RSO FD = 1.4		513
19	Ac/C18:0 MeRSO FD=1.1		638
20	Ac/ Bz MeRSO FD = 1.1		476
21	Ac/CH MeRSO FD = 1.1		482
22	Ac/iC18:0 MeRSO FD = 1.1		638
23	Ac/C18:2 MeRSO FD = 1.1		634
24	Ac/DEPA MeRSO FD = 1.1		523
25	Ac/PEG MeRSO FD = 1.1		415
26	DiAc laurate glycerol		359

- ***FD: functionalization degree. It corresponds to the initial double bond content of the substrate***

The modified oils are based on epoxidised soybean oil and epoxidised methyl esters from rapeseed and soybean oil supplied by Oléon and chemically modified in the UMR 5256 laboratory are resumed in the Table 3. All of the reactions were carried out under nitrogen atmosphere. The products were identified on the basis of their ^{1}H NMR catalysis (Bruker AV 250Hz).

- ***Epoxidation (compounds 10 and 11)***

In a 100 ml round bottom flask, 4g of SBO **6** were stirred at room temperature in the presence of HCOOH (0.014 ml of concentrated HCOOH). 0.40 ml of H_2O_2 (30%, 1.1 eq./ Triglyceride vegetable (TGv)) was added dropwise. The mixture was stirred at 70 °C for 24h. After cooling to room temperature, 20 ml of Et_2O was added and the organic phase was washed with 20ml H_2O, 20 ml saturated Na_2CO_3 and 20 ml saturated NaCl, then dried over $MgSO_4$ and the solvent was evaporated. 80% wt. of epoxidised methyl oleate was obtained.
NMR analysis indicated around 1.5 epoxide /TG 10. ^{1}H NMR ($CDCl_3$, 250 MHz) δ ppm: 0.8 (9H), 1.2–1.6 (58H), 1.6 (6H), 2.2 (6H), 2.8–3.2 (3H), 4.2 (4H), 5.1 (10H). Similarly, in the presence of 2.2 of H_2O_2 / TG, 2.5 epoxides / TG 11 are obtained. ^{1}H NMR ($CDCl_3$, 250 MHz) δ ppm: 0.8 (9H), 1.2-1.6 (58H), 1.6 (6H), 2.2 (6H), 2.8-3.2 (6H), 4.2 (4H), 5.1 (7H).

- ***Symmetric esters (compounds 16–18)***

In a 20 ml round bottom flask, 1 g of epoxidised methyl ester of soybean oil **15** (3.2 mmol, corresponding to 3.9 mmol epoxide) was reacted with 0.48 g of acetic anhydride (4.7 mmol) in the presence of 53 mg of tetrabutylammonium chloride (0.2 mmol, 5%). The mixture was stirred at 130 °C for 6 h. After cooling to room temperature, 10 ml of Et_2O were added and the organic phase was washed with 10 ml H_2O, 10 ml saturated Na_2CO_3 and 20 ml saturated NaCl, then dried over $MgSO_4$ and the solvent evaporated. 100 mol% of slightly yellow diAc methyl ester of soybean oil **16** was obtained. ^{1}H NMR ($CDCl_3$, 250 MHz) δ ppm: 0.8 (t, 6.6 Hz, 3H), 1.2 (m, 19H), 1.5 (m, 4H), 2.0 (s, 6H), 2.2(t, 7.5 Hz, 2H), 3.6 (s, 3H), 4.7 (m, 2H).
In a 20 ml round bottom flask, 1 g of epoxidised methyl ester of soybean oil **15** (3.2 mmol corresponding to 3.9 mmol epoxide) was reacted with 0.79 g of benzoic anhydride (3.5 mmol) in the presence of 53 mg of tetrabutylammonium chloride (0.2 mmol, 5%). The mixture was

stirred at 130 °C for 6 h. After cooling to room temperature, 10 ml of Et_2O were added and the organic phase was washed with 10 ml H_2O, 10 ml saturated Na_2CO_3 and 20 ml saturated NaCl, then dried over $MgSO_4$ and the solvent evaporated. 80% diBz methyl ester of soybean oil **17** was obtained. ^{1}H NMR (CDCl3, 250 MHz) δ ppm: 0.8 (m, 3H), 1.2 (m, 19H), 1.6 (m, 6H), 2.2 (m, 2H), 3.6 (s, 3H), 5.3 (m, 2H), 7.4 (m, 4H), 7.5 (m, 2H), 7.9 (m, 4H).

Ethylhexyl rapeseed ester was epoxidised using the first set of conditions and reacted with acetic anhydride using the same conditions to obtain a 94 mol% yield of **18** (yellow oil). ^{1}H NMR (CDCl3, 250 MHz) δ ppm: 0,8 (9H), 1,2 (19H), 1,5 (4H), 2,0 (5H), 2,2 (2H), 4,9 (1,7H).

- ***Dissymmetric esters***

The reaction was carried out in a 20 ml closed vial equipped with a magnetic stirrer. A mixture of 3 g (10.5 mmol of epoxide) of epoxidised methyl ester of soybean oil **15**, 1.41 g (12.6 mmol, 1.2 eq.) of benzoic acid and 5% of tetrabutylammonium chloride were introduced into the vial. The reaction mixture was heated to 130 °C under stirring for 6 h, then 2 eq. of acetic anhydride (4.7 g) were added dropwise and the mixture stirred overnight. After cooling, the mixture was diluted with Et_2O, washed with water, saturated Na_2CO_3 and saturated NaCl solution. The organic layer was dried over $MgSO_4$ and after evaporation of the solvent the product **20** was isolated as a viscous orange oil (80%). ^{1}H NMR (CDCl3, 250 MHz) δ ppm: 0.8 (m, 3H), 1.2 (m, 19H), 1.5 (m, 6H), 2(m, 3H), 2.2(m, 2H), 3.6 (s, 3H), 5.1 (m, 2H), 7.4(m, 2H), 7.5(m, 1H),8(m, 2H).

Using a similar protocol, 95 mol% yield of a slightly yellow oil **21** was obtained. ^{1}H NMR ($CDCl_3$, 250 MHz) δ ppm: 0.8 (m, 3H), 1.2 (m, 22H), 1.4-1.6 (m, 8H), 1.7 (m, 2H), 1.8 (m, 2H), 2 (m, 3H), 2.2 (t, 7,7Hz, 2H), 3.6 (s, 3H), 5.1 (m, 2H).

Using a similar protocol, 68 mol% yield of a viscous oil **22** was obtained. ^{1}H NMR ($CDCl_3$, 250 MHz) δ ppm: 0.8 (t, 6,7Hz, 9H), 1.2 (m, 38H), 1.5-1.6 (m, 8H), 2.0 (s, 3H), 2.2 (m, 4H), 3.6 (s, 3H), 5.0 (m, 2H)

Using a similar protocol, 58 mol% yield of a viscous oil **23** was obtained. ^{1}H NMR ($CDCl_3$, 250 MHz) δ ppm: 0.8 (t, 7,0Hz, 3H), 0.9 (t, 7,6Hz, 3H), 1.2 (m, 33H), 1.5 (m, 8H), 2.0 (s,3H), 2.2 (t, 7,3Hz, 4H), 2.7 (m, 2H), 3.6 (s, 3H), 5.0 (m, 2H), 5.3 (m, 4H).

Using a similar protocol, 84 mol% yield of a colourless viscous oil **24** was obtained. ^{1}H NMR ($CDCl_3$, 250 MHz) δ ppm: 0.9 (m, 3H), 1.2 (m, 20H), 1.6 (m, 6H), 2.0 (m, 6H), 2.3 (m, 2H), 3.6 (s, 3H), 4.2 (m, 1H), 5.0 (m, 2H).

- ***Ether-ester***

A mixture of 3 g (10.5 mmol epoxide) of epoxidised methyl ester of soybean oil **15**, 8.5 g of PEG (poly ethylene glycol) 200 (4 eq.) and 0.01 g of $BF_3.OEt_2$ were stirred for 3 h at room temperature. After cooling, the mixture was diluted with Et_2O, washed with water, saturated Na_2CO_3 and then saturated NaCl solution. The organic layer was dried over $MgSO_4$ and the solvent was evaporated. The product was acetylated in the presence of Ac_2O for 24 h at 130 °C, and the same purification was used. A 76% yield of **25** was obtained over the two steps. ^{1}H NMR ($CDCl_3$, 250 MHz) δ ppm: 0.8 (3H), 1.2 (18H), 1.5 (7H), 1.9 (5H), 2.2 (2H), 3.2 (1H), 3.5 (12H), 4.1 (1H), 4.8(1H).

- ***Acetylation of glyceryl laurate***

In a 50 ml round bottom flask, 3 g of glyceryl laurate (10.9 mmol) was reacted with 2.70 g of acetic anhydride (26.2 mmol, 1.2 eq.) at 130 °C for 24 h. After cooling to room temperature, 10 ml of Et_2O were added and the organic phase was washed with 10 ml H2O, 10 ml saturated Na_2CO_3 and 20 ml saturated NaCl, then dried over $MgSO_4$ and the solvent evaporated. A 90% yield of colourless diAc laurate glycerol **26** was obtained. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 0.8 (6H), 1.2(14 H), 1.5 (2H), 2.0 (6H), 2.2 (2 H), 4.0 (2H), 5.1 (1H)

a) Oil diffusion process probed by rheology

First of all, the temperature dependence of the viscosity of the oils was measured on a stress rheometer (AR 2000 from TA). The samples were tested using a shear steady regime ($10s^{-1}$) at 20, 40, 60, 80, 100 and 120 °C. It was observed that all the oils obey the Arrhenius law according to the equation:

$$\eta_0 = Aexp\left[\frac{E_a}{RT}\right] \quad (11)$$

Where E_a is the flow activation energy. The values of the flow activation energies are reported in the following tables 4 and 5.

- ***Diffusion in EPDM***

The principle of the rheological experiment for the study of the diffusion of plasticiser in a molten polymer was described in our previous papers [36-39]. The principle of this method is shown in Figure 3 with the evolution of diffusion of oil in sample in function of the variation of absolute complex modulus viscosity during time. A layer of liquid is placed on the top of a layer of molten polymer and the complex shear modulus ($G^*(\omega)=G'(\omega)+jG''(\omega)$, $j^2=-1$) of the assembly at a constant frequency is measured as a function of time. We will consider the variation of the absolute complex viscosity, here named viscosity for purposes of convenience.

$$|\eta*(\omega)| = \sqrt{\frac{G'^2}{\omega^2} + \frac{G''^2}{\omega^2}} \quad (12)$$

At the early stages of diffusion, the viscosity of the bi-layer is low since it is dominated by the fluid of lower viscosity. The viscosity of the bilayer increases slowly until the polymer layer, swelled by the fluid, occupies all the gap. In the intermediate stages, the diffusion of the low molar mass molecule across the polymer layer creates a gradient of concentration that induces viscosity variations. The global viscosity of the sample rises and finally, at the end of the diffusion process the viscosity reaches a stable value as the system is definitively homogenous (plasticised polymer). Consequently, the viscosity varies considerably from the viscosity of the liquid-plasticiser at the beginning of the diffusion process to the viscosity of the polymer–liquid homogeneous medium at the end of the diffusion process. Therefore, the variation in the viscosity can be related to the transport behaviour of the polymer–liquid system.

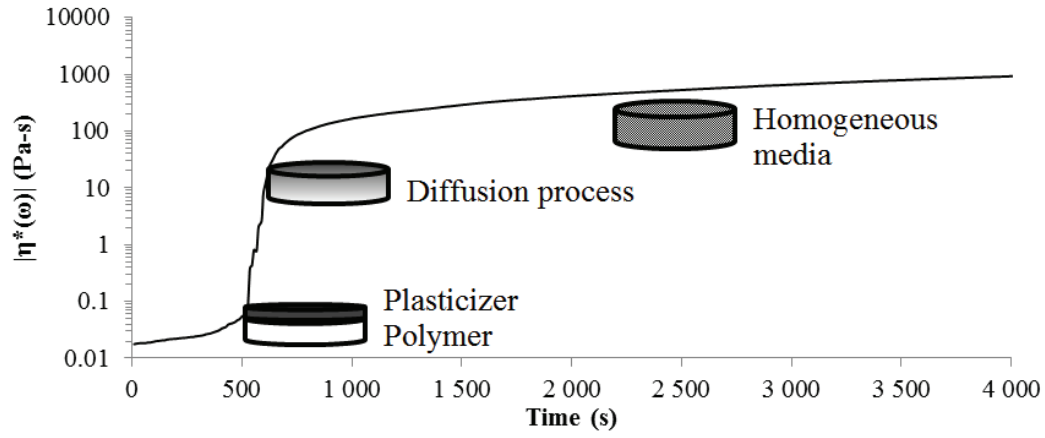


Figure 3. Illustration of the variation of the absolute complex modulus viscosity versus time due the progress of the mineral oil (Torilis® 7200) diffusion in a molten EPDM (Vistalon® 8800) layer at 160°C (ω=10 rad s^{-1}).

In our previous studies [37, 40], we showed that the molten polymer and solvent behave like purely viscous fluids. Consequently, the mass transport can be described by the classical Fick's second law of diffusion:

$$\frac{\partial C}{\partial t} = \nabla D_{12} \nabla C \quad (13)$$

where C is the concentration of the diffusing molecule. D_{12} is the mutual diffusion coefficient that depends strongly on the concentration of the diffusing molecule [40]. The Flory–Huggins theory enables the binary mutual diffusion coefficient D_{12} to be obtained from the solvent self-diffusion coefficient D_1. The expression of the former above the glass temperature is then:

$$D_{12} = D_1(1-\phi_1)^2(1-\chi\phi_1) \quad (14)$$

with ϕ_1 the volume fraction of the solvent in the polymer and χ the Flory–Huggins interaction parameter, respectively. By definition:

$$\chi = \frac{\upsilon_{molar}}{RT}\left(\delta_{solvent} - \delta_{polymer}\right)^2 \quad (15)$$

These equations prove that the diffusion is controlled by the solubility parameters and the free volume (variation of D_1 with the temperature). If V^* is the minimum volume hole size into which a molecule of penetrant can jump and V_{FH} the average free volume, the self-diffusion coefficient can be then considered proportional to the probability of finding a hole of V^* or larger:

$$D_1 = A\exp(-\gamma V^*/V_{FH}) \quad (16)$$

where γ is a numerical factor between 0.5 and 1 that is introduced to account for the overlap between free volume elements. A is a constant of proportionality related to the gas kinetic velocity.

From inverse rheological methods, the mutual diffusion coefficient can be calculated [37]. However, in the present study the diffusion curves have only been compared from a qualitative point of view.

From an experimental point of view, the following protocol was followed for the diffusion experiments. The EPDM polymer disk (1mm thick) was placed on the lower plate (diameter: 50mm) of the rheometer (AR2000 from TA) in a pre-heated oven for a few minutes. The plasticiser was injected between the polymer sample and the upper plate using a syringe. The plasticiser gap was adjusted to diffuse the equivalent of 20% wt. of plasticiser. The variation

of the dynamic modulus G' and G'' and consequently of the absolute complex viscosity $|\eta^*(\omega)|$ during the diffusion of the oil into the polymer matrix was followed by time sweep oscillatory shear experiments (ω= 10 rad/s) at a given temperature. The strain amplitude was manually adjusted (from 400 to 1%) during the test in order to maintain the torque at a measurable level at the beginning and remain within the domain of linear viscoelasticity. Furthermore, if efficient diffusion was observed where the oil and polymer formed a homogenous medium, a frequency sweep oscillatory shear experiment was performed at the end of the experiment at the same temperature.

- ***Diffusion in PVC Plastisols***

A different rheological method was used to probe the diffusion of plasticisers in a suspension of PVC grains (PVC plastisol). In a previous study [41], we showed that oscillatory shear experiments can be successfully used to study the diffusion of plasticisers in PVC grains. Furthermore, this method was successfully developed to study the diffusion of different plasticisers in starch grains [42].

Experimentally, the plastisol was introduced between the plates (thickness: 1 mm; diameter: 25mm) of the rheometer (AR2000 from TA). The plastisol was heated from 20 °C to 160 °C with a controlled ramp of 5 °C/min. The frequency of 6.283 rad/s was used to measure the variation of the viscoelastic behaviour versus the time of diffusion. To remain in the linear domain we decided to use a constant strain of 0.3%. This average value is a compromise between signal strength and linearity, this compromise allowed to obtain the curve as the Figure 4.

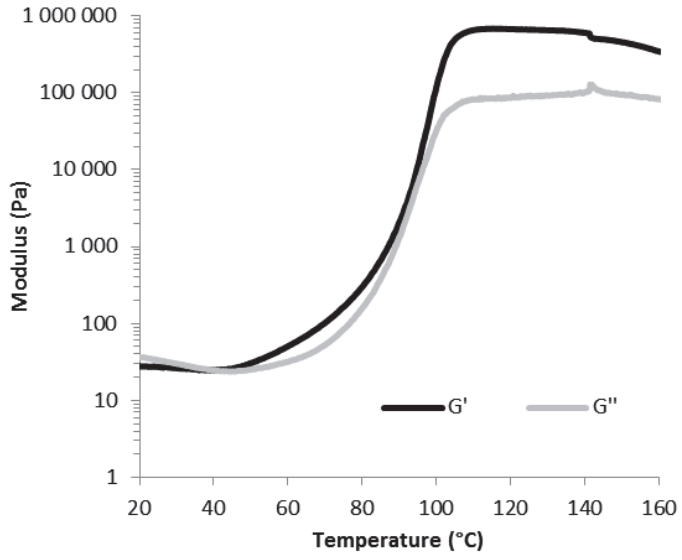


Figure 4. Variation of the complex shear modulus versus temperature for a plastisol with a formulation of 30%wt of DINP (ω=6.283 rad.s^{-1}, Temperature ramp: 5°C min^{-1}).

From the typical curves shown in Figure 4, information concerning the diffusion process of the plasticiser can be obtained. At low temperatures (<40 °C), the viscosity decreases, as the rheology is governed by the viscosity of the plasticiser. The value of this viscosity is extremely important in terms of PVC applications and plastisol storage at room temperature. In the temperature range 40–120 °C, the pre-gelation zone is observed when the plasticiser penetrates into the PVC grains. PVC grains aggregate and start to interpenetrate during this second step. Above 120°C the plasticised PVC grains interpenetrate (diffusion of PVC chains) to form a homogeneous medium and the material has good cohesion. It can be noted that the term of gelation does not define a brutal transition between two states, liquid and solid for example. Instead, it is a progressive phenomenon, which comprises all of the structural changes that the grains of PVC undergo during the process from their initial powder state to their final state as a physical gel. However, a PVC plastisol does undergo a sol–gel phase transition due to the percolation of the grains of PVC, which is a physical gelation. Consequently, it is necessary to keep in mind the difference between the gelation process and the sol–gel transition (physical gelation) [41].

To conclude, it is possible to obtain relevant information from these curves from a qualitative point of view. Furthermore, the acetone test, consisting of the immersion of plasticised PVC samples in acetone for 24 hours has been used to check the homogeneity and cohesion of the PVC samples at the end of this diffusion process.

III- Results and discussion

a) EPDM/oils systems

The determination of the most suitable oils for the EPDM was performed by analysing different factors dominating in the Fick law through the mutual coefficient of diffusion and consequently the solubility parameters according to Equations 12–16. Soybean oil was the first unmodified oil tested and was used as a reference. In the second step, each modification carried out on this oil contributed to understanding the mechanisms of diffusion and solubility in order to determine the ideal candidate using a molecular design point of view.

Table 4. Plasticizers for EPDM matrix with their viscosity at 20°C and 160°C, the rate of solubility at 20°C, the Hansen solubility parameters, the activation energy and their values of RED for Vistalon® 8800 matrix.

	Name/ Reference	Solubility at 20°C (% of weight)	δ_D MPa$^{1/2}$	δ_p MPa$^{1/2}$	δ_h MPa$^{1/2}$	δ_t MPa$^{1/2}$	Viscosity at 20°C (Pa.s)	Viscosity at 160°C (Pa.s)	Ea kj/mol	R_a	RED R_a/R_0
	EPDM		18.2	1.9	2.0	19.5				Ro= 7.2	
Triacyl glycerol	**Torilis® 7200**	Soluble	19.8	0.8	5	20.5	1.57	4.1×10^{-2}	73	4.38	0.61
	Soybean oil / 6	12.1	16.4	4.7	3	17.3	9.0×10^{-2}	1.3×10^{-2}	12.4	4.80	0.67
	Safflower oil / 7	11.2	15.4	3.3	5.7	16.7	8.0×10^{-2}	3.3×10^{-2}	20.4	6.99	0.97
	Linseed oil / 8	18.6	17.2	4.2	3.4	18.1	9.0×10^{-2}	2.2×10^{-2}	25.7	3.45	0.48
	Tung oil / 9	11.9	16.7	5.7	5.8	18.5	2.8×10^{-1}	1.0×10^{-2}	27.8	6.22	0.86
Epoxides	**15**	0	15.9	5.5	5.0	17.5	5.0×10^{-2}	9.0×10^{-3}	10.3	6.68	0.93
	10	0	16.3	5.5	2.9	17.4	1.1×10^{-1}	3.0×10^{-2}	17.5	5.43	0.75
	12	0	15.6	6.6	3.7	17.3	6.6×10^{-1}	1.1×10^{-2}	25.5	7.33	1.02
FAME	**14**	Soluble	16.6	2.4	3.6	17.1	3.0×10^{-2}	1.0×10^{-3}	11.6	3.76	0.52
	13	Soluble	16.3	2.4	3.2	16.8	6.0×10^{-3}	2.0×10^{-3}	11	4.18	0.58
Dissymetric esters	**23**	13.1	16.2	2.5	2.7	16.6	2.1×10^{-1}	3.1×10^{-2}	12.2	4.27	0.59
	22	25.6	16.1	2.1	2.4	16.4	1.6×10^{-1}	3.3×10^{-2}	15.5	3.59	0.50
	19	No data	16.3	2.3	2.6	16.7	Ø	Ø	Ø	4.04	0.56

*FAME Fatty acid methyl ester

To predict the compatibility of the plasticiser and the EPDM, we first measured the solubility parameters of the EPDM and the oils. The data in Table 4, as expected, show that the polar component $\delta_p<2.0$ has a small contribution in the EPDM, the dispersive component $\delta_D=18.2$ MPa$^{1/2}$ being the major contributor and the global solubility parameter having a value of

δ=19.5 $MPa^{1/2}$. The value of the radius interaction of EPDM is R_0=7.2. Comparing this value with the database associated with the HSPiP software, it can be seen that this value is low for a polymer. Consequently, a solvent fluid must have a solubility parameter close to the solubility parameter of EPDM. Therefore, obtaining a bio-plasticiser with a low contribution from the polar component is a challenge [43], as the bio-molecules are often composed of several polar atoms. In this case, triacyl glycerol, epoxides and FAME present a polar component that is too high to enhance the compatibility with EPDM. Thus, to promote compatibility between EPDM and the plasticisers, it is important to reduce the polar function in the vegetable oil molecules. With this aim, the dissymmetric esters were synthesised. Furthermore, from a quantitative point of view, it is important to understand all of the factors influencing miscibility and diffusion in the EPDM matrix.

The viscosities at two temperatures (T=20 °C and 160 °C) and the energy activations in this range of temperatures are reported in Table 4. Compared with the Torilis® oil, the activation energy of all of the vegetable oils was low (10<Ea (kJ/mol) <30) showing a low dependence of the viscosity on temperature. However, the rheological curves show two distinct diffusion behaviours as shown in Figure 5. At T=100 °C, the oil diffusion process, whatever the nature of the oil (shown here only for Torilis® oil), is extremely low compared with the diffusion at temperatures higher than 120 °C. It can also be observed that the dependence of the diffusion on the temperature is low above 120 °C, as can be expected from the activation energies of the oils (70 $kj.mol^{-1}$ Torilis®). To explain the discontinuous behaviour of the diffusion process around 110 °C, it should be noted that EPDM has a residual micro-crystallinity which melts at a temperature close to 110 °C, this crystallinity having already been highlighted in a previous study [44]. Consequently, the diffusion of the vegetable oils was studied at a temperature of 160 °C in the subsequent parts of the study.

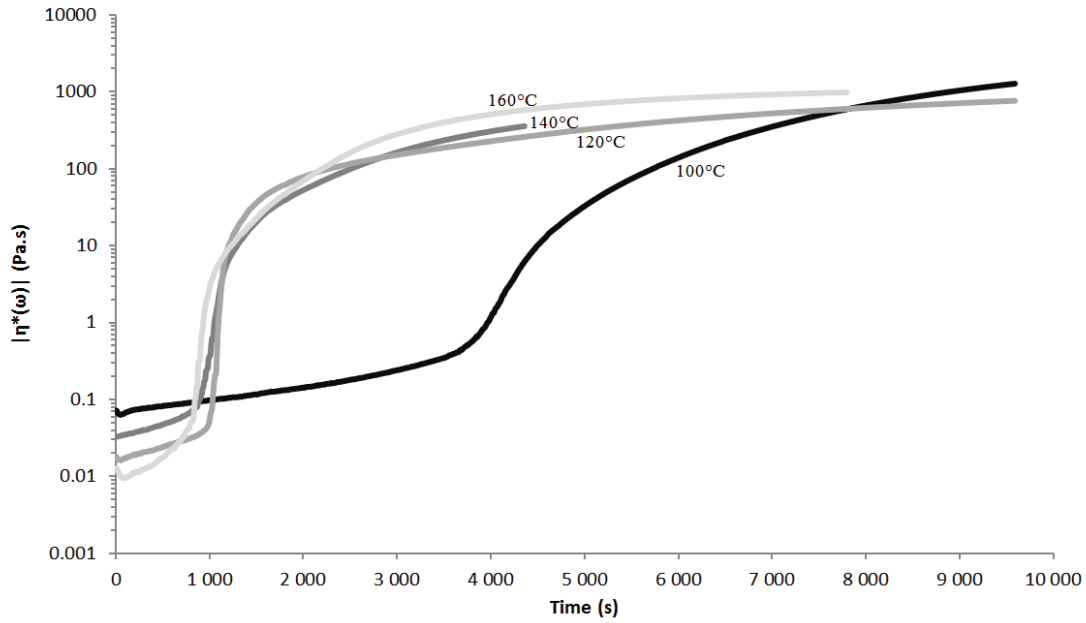


Figure 5. Diffusion of the Torilis® oil (Mineral oil) in EPDM. Variation of the absolute complex viscosity $|\eta^*(\omega)|$ versus time (ω=10 rad s^{-1}) at different temperatures.

- ***Influence of the nature of the vegetable oil and the iodine value***

Figure 6**Figure 6** shows the diffusion process of different vegetable oils in EPDM at T=160 °C. The diffusion curve of the Torilis® oil was used as the standard reference. As can be observed, the epoxidised methyl ester of soybean oil (MeESBO) **15** does not diffuse in EPDM. The safflower oil displays very similar diffusion properties to the Torilis® oil and the soybean methyl ester of soybean oil (MeSBO) **14** diffuses faster than the Torilis® oil. However, these differences in diffusion cannot be explained in terms of solubility parameters through the relative energy difference (RED defined in Equation 10, values in Table 4). In fact, the values for the RED parameters are not in agreement with the experimental diffusion results. For example, the safflower oil **7** and epoxidised methyl ester of soybean oil (MeESBO) **15** have similar values of RED (0.97 and 0.93, respectively) whereas their rheological diffusion curves show opposite behaviour, as explained above. However, if we consider the unsaturation number of these oil molecules and use the iodine classification [45], we find the following hierarchy: soybean oil **6** > safflower oil **7** > linseed oil **8**, which shows no relation with the diffusion speed. Unfortunately, it seems that this type of analysis remains too qualitative as it does not take into account the complexity of the oil molecules in terms of their architecture, molar mass and chemical structure.

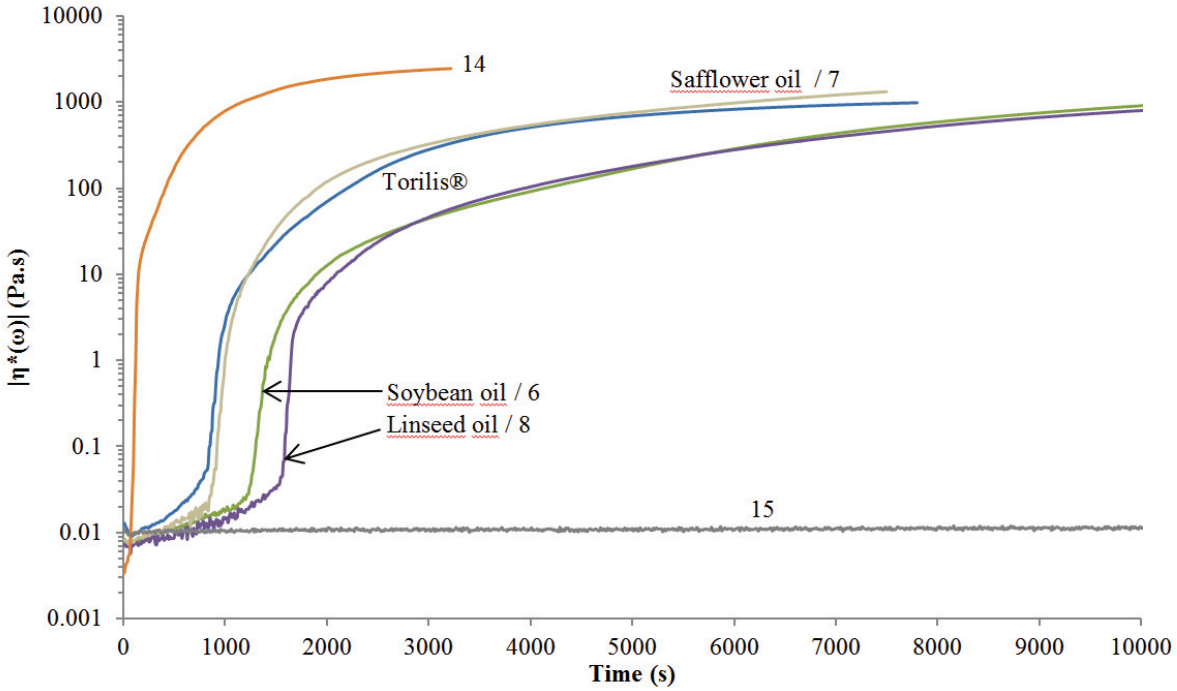


Figure 6. Diffusion of different vegetable oils in EPDM at T=160°C. Variation of the absolute complex viscosity |η*(ω)| versus time

Actually, as expressed by the equation of the mutual diffusion coefficient, the solubility parameters cannot be the only factors that predict the diffusion power of vegetable oils. As shown by Equation 14, diffusion is related both to solubility parameters and to the self-coefficient D_1. D_1 is generally derived from the free volume theory (temperature dependence) taking into account the front factor A of Equation 16, the molar mass of the diffusing liquid, through its viscosity. To understand and to show the influence of these different parameters on the diffusion process we studied these rheological diffusion curves separately and in more detail.

- ***Influence of the polarity parameter δp***

The polarity of soybean oil (SBO) **6** and methyl ester of soybean oil (MeSBO) **14** were modified by the introduction of chemical groups via epoxidation to give epoxidised soybean oil (ESBO) **12** and epoxidized methyl ester of soybean oil (MeESBO) **15**. It should be noted that the epoxidation treatment changes the molar mass of the molecules only slightly. As a result, it can be observed in Table 4 that δ_p drastically increases, and consequently the RED coefficient as well, with the epoxidation of the vegetable oils. For example, the polarity parameters of the methyl ester of soybean oil **14** and the epoxidized methyl ester of soybean

oil **15** are δp=2.4 and 5.5 $MPa^{1/2}$, respectively. It must be borne in mind that EPDM can be considered as a non-polar polymer, since its polarity parameter is 1.9$MPa^{1/2}$. As predicted from the polarity difference between the ester and the epoxidised ester, Figure 7a shows that the soybean oil diffuses whereas the epoxidised soybean oil does not diffuse, whatever the degree of epoxidation (partially epoxidised **10**, **11** and fully epoxidised soybean oil **12**; see in Table 3). The same behaviour is observed in Figure 7b for the methyl ester of soybean oil **14** and its epoxide derivative **15**. It can be concluded, then, that the polarity of some chemical functional groups, such as the epoxy group in this case, plays an important role in the diffusion ability of vegetable oils.

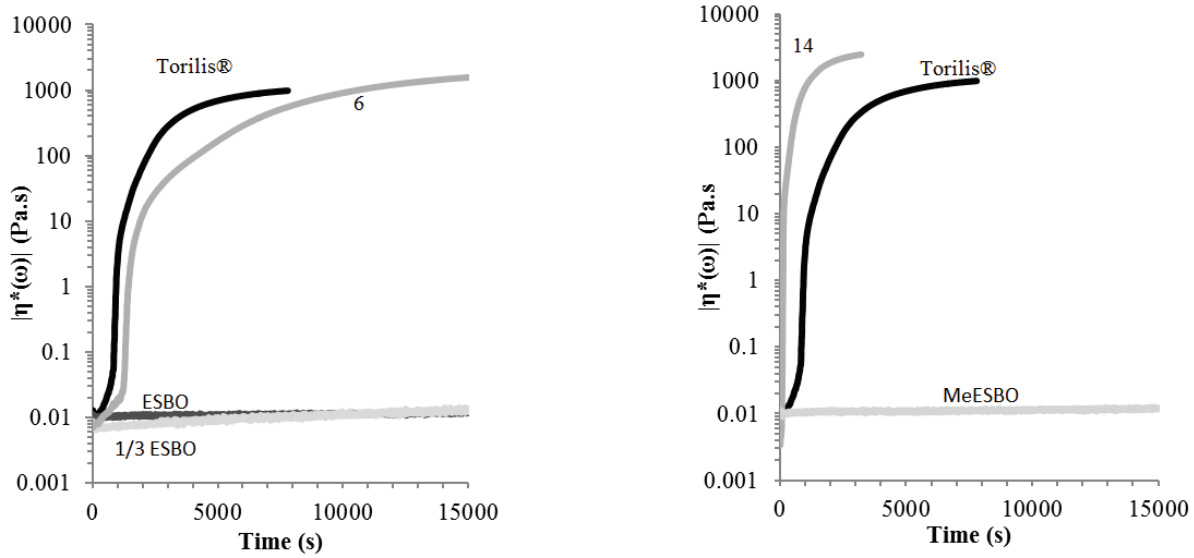


Figure 7. Influence of the polarity parameter on the diffusion of vegetable oils. Variation of the absolute complex viscosity |η*(ω)| versus time at T=160°C. The diffusion of the Torilis® curve is used as reference only.

a) Diffusion of soybean oil (δ_p=4.7 $MPa^{1/2}$) and its epoxide derivatives(1/3 ESBO: δ_p=5.5 $MPa^{1/2}$, ESBO: δ_p=6.6 $MPa^{1/2}$)
b) Diffusion of methyl ester of soybean oil (δ_p=2.4 $MPa^{1/2}$) and its epoxide derivative (MeESBO: δ_p=5.5 $MPa^{1/2}$)

- ***Influence of the oil molar mass***

To study the influence of the molar mass, we used the soybean (M≈900g.mol-1) and methyl ester of soybean oil (M≈300g.mol-1) vegetable oils. Their viscosities were 1.1x10^{-2} and 1.0x10^{-3} Pa.s respectively at T=160°C. The chemical structure of these two molecules is extremely close and we calculated δt=17.3 and δt=17.1 $MPa^{1/2}$, respectively. As shown in Figure 1 and Figure 8, as expected from the difference in molar masses, the methyl ester of soybean oil (MeSBO) **14** diffuses faster in EPDM than the soybean oil (SBO) **5**. Theoretically, according to Equations 12–16 the viscosity of the diffusing liquid (contained in

the front factor A of Equation 16) is the dominant factor, as the interaction parameters change only slightly between the two molecules and their activation energies are extremely close (12.4 and 11.6 kJ mol^{-1}, respectively). In other words, the variation of the mutual diffusion coefficient D12 is only due to the variation in the front factor A in the present system.

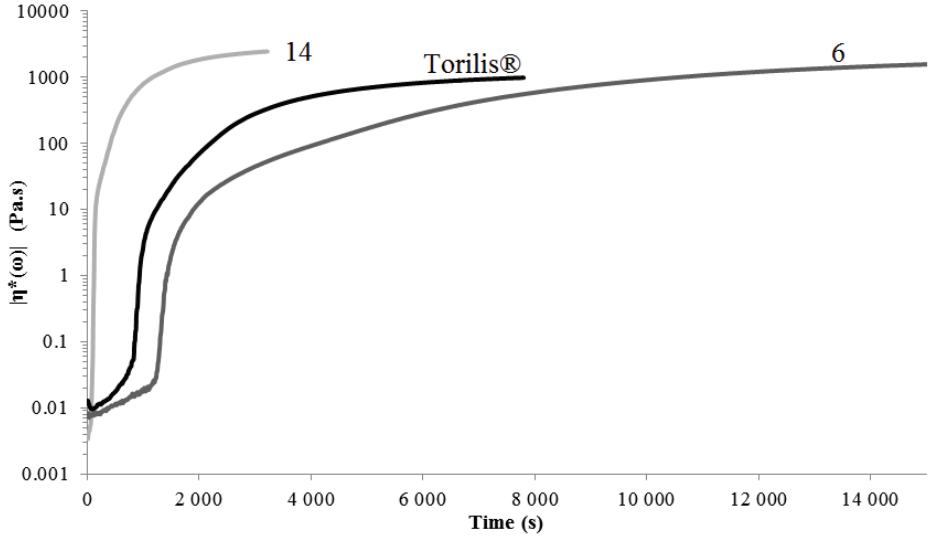


Figure 8. Influence of the molar masses on the diffusion of vegetable oils 6 and 14. Variation of the absolute complex viscosity $|\eta^*(\omega)|$ versus time at T=160°C. The diffusion of the Torilis® curve is used as reference only.

- ***Influence of the molecular architecture***

The molecular architecture could also have an influence on the diffusion process [46-48]. To study the influence of the molecular structure on the diffusion, we synthesised similar substrates containing either a long linear chain **23** or a branched chain **22**. Although both of these molecules had extremely similar solubility parameters (δ_t=16.6 and δ_t=16.4 $MPa^{1/2}$), viscosities ($3.3x10^{-2}$ and $3.0x10^{-2}$ Pa.s) and energy activations (12.2 and 15.5 $kJmol^{-1}$), their rheological diffusion curves showed significantly different behaviour. However, in terms of diffusion these molecules displayed the same behaviour with respect to the slope of the variation of the viscosity for experimental times shorter than 400s, according to Figure 9. In fact, the difference in their behaviour was due to their final viscosity values ($6.0x10^{2}$ and $2.0x10^{4}$ Pa.s, respectively). It was observed during the experiment that the linear molecule does not diffuse totally in EPDM and consequently, a non-homogeneous sample was observed at the end of the experiment. The solubility test, as shown in Table 4, shows that the branched molecule was twice as soluble as the linear one. However, this solubility was measured at the room temperature and is not necessary representative of the solubility at T=160°C.

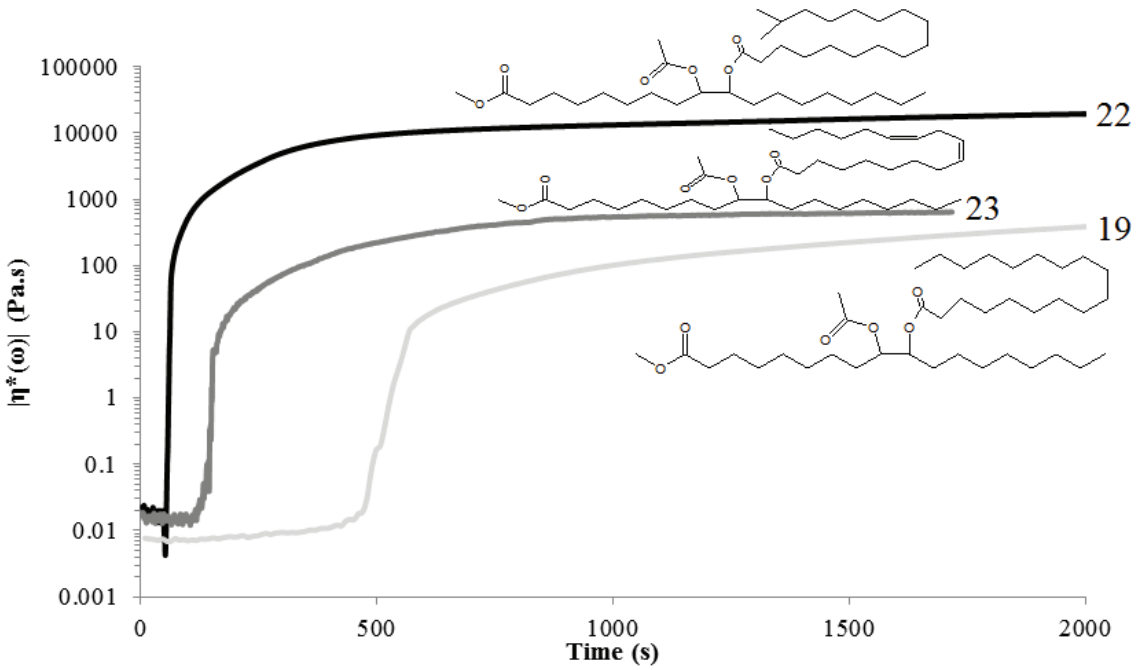


Figure 9. Influence of the molecular architecture on the diffusion process. Variation of the absolute complex viscosity |η*(ω)| versus time at T=160°C. The Lino/Ac linear molecule does not lead to a homogeneous sample.

From this result, we could conclude that for molecules with similar viscosity and chemical properties, the most branched geometry is the most favourable plasticiser, which is in contradiction with previous studies [44, 47]. However, this behaviour cannot be generalised and extended to other systems without a more fundamental understanding of the underlying mechanism.

b) PVC/Oil plastisol systems

PVC suspensions (PVC grains in suspension in plasticiser fluid) for industrial plastisol applications have to meet some specific requirements. From a processing point of view, the plasticiser must have a viscosity much lower than 10^{-2}Pa.s at room temperature in order to generate a suspension with a viscosity lower than 10Pa.s. Furthermore, diffusion of the plasticiser in PVC grains at room temperature, i.e. the plasticising power, must not occur, in order to produce time-stable suspension for the storage of the formulation. In other words, the plasticiser must not be a good solvent for the PVC grains at room temperature. For example, soybean oil diffuses in PVC grains at room temperature, and consequently could not be used as PVC plasticiser for plastisol applications. Its derivative molecules probably behave similarly. In addition, the viscosities of soybean oil and its derivatives are much higher than

10^{-2} Pa.s. Finally, for commercial applications, the plasticisers must be colourless and odourless. Another extremely important point is the environmental stability of PVC materials derived from plastisol formulations. Taking into account all these parameters, our study was focused on the most promising vegetable oil (MeSBO) and its derivatives obtained by chemical modification. DINP was used as the standard reference for the plasticiser and the final objective was to design a vegetable oil molecule that could mimic the properties of DINP. For that purpose, we analysed the solubility parameters and behaviour in rheological experiments of molecules derived by chemical modifications of the epoxidized methyl ester of soybean oil (MeESBO) **15** and epoxidized methyl ester of rapeseed oil.

Figure 10 shows the variation of the absolute complex viscosity versus temperature for methyl ester of soybean oil **14** and the modified MeSBO molecules, diAc MeSBO **16** and diBz MeSBO **17**, respectively (see Table 3 for their chemical structures). As explained in the experimental section, such rheological experiments allow us to study the gelification of PVC plastisols. The rheological curve of the diAc MeSBO **16-**based suspension is very close to the behaviour of the DINP suspension. All of these molecules have solubility parameters in the range: $17.1 < \delta_t$ ($MPa^{1/2}$) < 17.7, close to the value for DINP (δ_t = 17.4$MPa^{1/2}$). The values of the components of the solubility parameter are detailed in Table 5**Table 5**. From analysis of the polarity parameter, the following plasticising power can be determined: diBz MeSBO **17**(δ_p =6.3$MPa^{1/2}$) > DINP **4** (δ_p =5.1$MPa^{1/2}$ > diAc MeSBO **16** (δ_p=3.3$MPa^{1/2}$) > MeSBO **14** (δ_p =2.4$MPa^{1/2}$). These results are in agreement with the rheological gelification curves. Actually, the methyl ester of soybean oil has a low viscosity but its gelification is delayed by 10 °C and the sample is brittle in the acetone test. Consequently, the methyl ester of soybean oil molecule has a low plasticising power as predicted by the polarity component. In terms of the solubility parameters (RED), the diBz MeSBO **17** molecule is the best plasticiser of all these molecules, with the lowest RED value (0.37). However, its viscosity is 2.7 Pa.s at room temperature and consequently this molecule is not suitable for use as a plastisol plasticiser. Furthermore, due to its high viscosity, the diffusion process above the T_g is delayed by few seconds. Finally, the diAc MeSBO **16** molecule is the best suitable molecule for application as a plasticiser as also indicated by its more similar behaviour to DINP **4**.

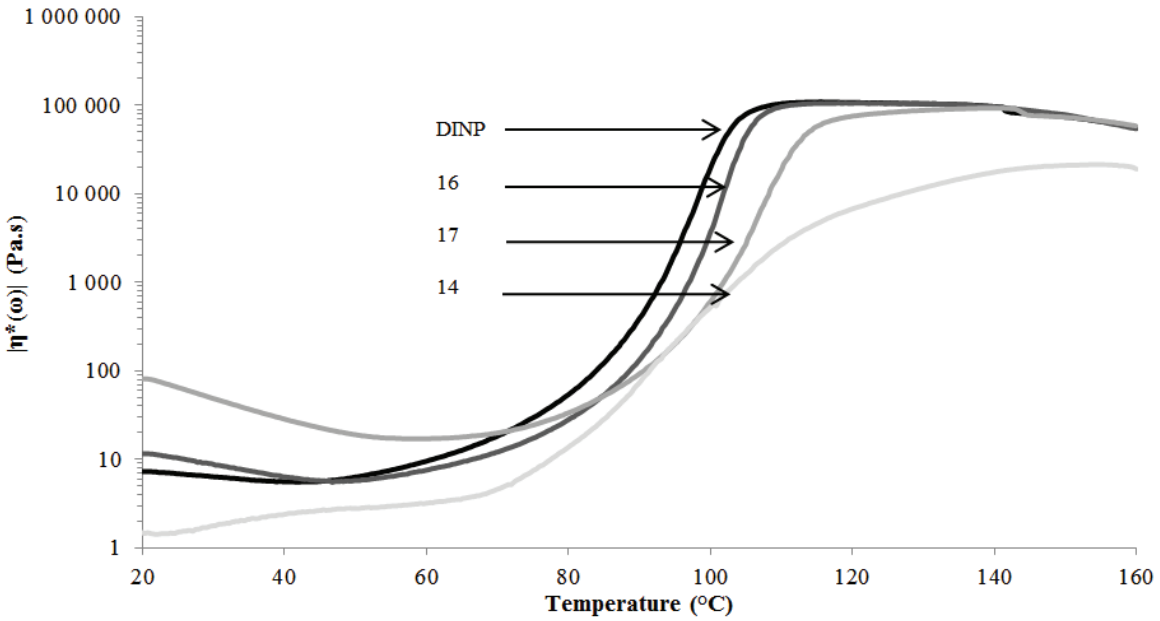


Figure 10. Gelification of plastisol PVC based on MeSBO molecules. Variation of the absolute complex viscosity |η*(ω)| versus temperature.

Table 5. Plasticizers for PVC matrix with their viscosity at 20°C and 160°C, the Hansen solubility parameters, the activation energy and their values of RED for Lacovyl® PVC matrix.

Name	δ_D $MPa^{1/2}$	δ_p $MPa^{1/2}$	$\delta_h MPa^{1/2}$	$\delta_t MPa^{1/2}$	Viscosity at 20°C (Pa.s)	Viscosity at 160°C (Pa.s)	E_a kJ/mol	R_a	RED R_a/R_0
PVC	17.6	7.8	3.4	19.5				Ro=8.2	
DINP	16.5	5.1	2.1	17.4	$2.7x10^{-2}$	$2.7x10^{-3}$	25.1	3.72	0.45
14	16.6	2.4	3.6	17.1	$3.0x10^{-2}$	$1.0x10^{-3}$	11.6	5.76	0.70
Soybean oil / 5	16.4	4.7	3.0	17.3	$9.0x10^{-2}$	$1.3x10^{-2}$	12.4	3.94	0.48
16	16.3	3.3	4.3	17.2	$8.0x10^{-2}$	$2.1x10^{-2}$	19.6	5.27	0.64
17	16.3	6.3	3.1	17.7	2.7	$4.1x10^{-2}$	40.6	3.02	0.37
20	16.4	4.5	3.5	17.4	$4.0x10^{-1}$	$3.4x10^{-2}$	25.0	4.08	0.50
21	16.6	2.9	3.5	17.2	$2.6x10^{-1}$	$3.4x10^{-2}$	32.1	5.29	0.65
24	16.4	8.2	6.3	19.4	$4.6x10^{-1}$	$4.6x10^{-3}$	36.5	3.79	0.46
25	15.4	4.7	5.3	17.0				5.71	0.70
18	16.3	2.5	3.1	16.8				5.91	0.72
26	16.4	4.0	5.4	17.7				4.92	0.60

One other set of oil molecules derived from the chemical modification of the methyl ester of soybean oil was also studied.

Among these molecules, the Ac/DEPA MeRSO **24** molecules had the closest solubility parameter (δ_t =19.4$MPa^{1/2}$) to PVC (δ_t =19.5$MPa^{1/2}$). Consequently, this molecule should be a good solvent for PVC. However, the cohesion test in acetone at the end of the gelification showed that the plasticised PVC had brittle properties due to weak inter-diffusion of PVC grains and Ac/DEPA MeRSO molecules. However, the molecule is extremely complex in terms of chemical modifications as it contains a phosphonate group. The three other molecules have solubility parameters in the range $16.8<\delta_t$ ($MPa^{1/2}$) <17.7 and polarity parameters in the range $2.5<\delta_p$ ($MPa^{1/2}$) <4.7. The plasticising power could therefore be predicted as: DiAc Laurate glycol **26** > Ac/PEG MeRSO **25** > DiAc isooctyl RSO **18**. Actually, **26** and **25** had extremely similar solubility parameters to that of DINP.

Nevertheless, the plasticised PVC with the Ac/PEG MeRSO **25** molecule did not show cohesive behaviour in the acetone test.

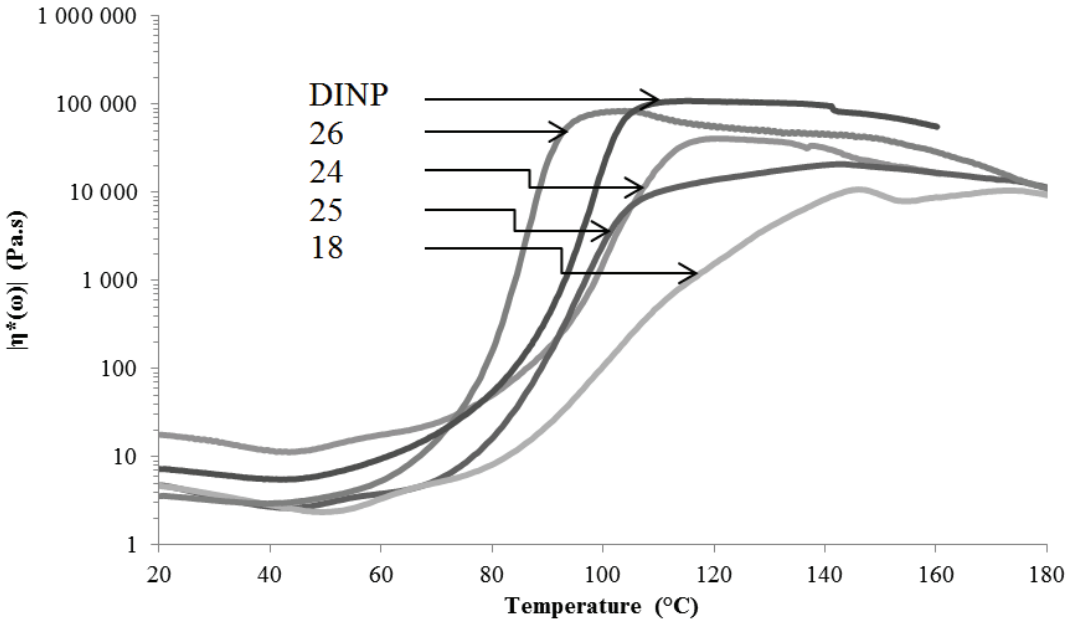


Figure 11. Gelification of plastisol PVC based on MeSBO molecules. Variation of the absolute complex viscosity

To conclude, the DiAc MeSBO **16** and DiAc Laurate glycol **26** molecules showed the best properties for plastisol applications (low viscosity, colourless, gelification curves and cohesive properties similar to DINP). However, these molecules have poor environmental stability in terms of their resistance to micro-organisms and their ageing under water conditions. To attempt to solve this problem, we considered another mixed functionalisation Ac/Bz MeRSO **20** and Ac/CH MeRSO **21** in order to improve the environmental stability of the molecules while maintaining the interesting plasticising properties of the Ac MeSBO oil. These new molecules had solubility parameters similar to DINP **4** (Ac/Bz MeRSO **20**: δ_t=17.2 $MPa^{1/2}$ and Ac/CH MeRSO **21**: δ_t=17.4 $MPa^{1/2}$). From the gelification curves shown in Figure 12**Figure 12**, the Ac/CH MeRSO oil **21** shows very similar behaviour to the DINP **4** plasticiser. Conversely, the gelation was delayed by 10 min for the Ac/Bz MeRSO oil molecule **20** and furthermore the sample was not cohesive in the acetone test.

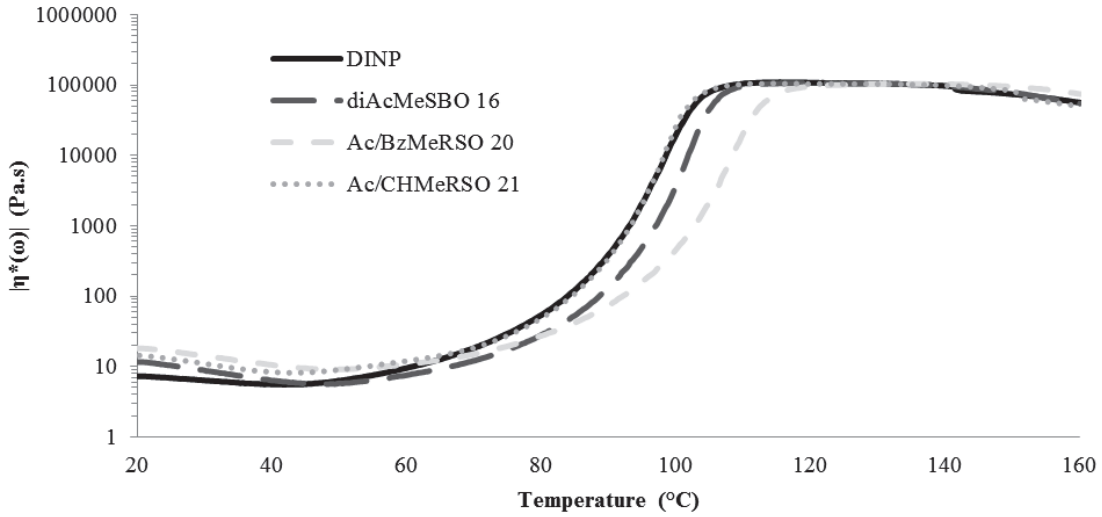


Figure 12. Gelification of plastisol PVC based on diAcMeSBO 16, Ac/BzMeRSO 20 and Ac/CHMeRSO 21 molecules. Variation of the absolute complex viscosity versus temperature.

IV- Conclusion

The objective of this work was to study the diffusion of some vegetables oils in EPDM and PVC (PVC plastisol). Furthermore, some of these raw vegetable oils, especially soybean oil, were chemically modified in order to improve their diffusivity and solubility in EPDM and PVC. All of these oils were characterised in terms of chemical structure, viscosity (and flow energy activation), and Hansen solubility parameters. An additional objective was to design new vegetable oil molecules able to mimic fossil molecules such as mineral oil (Torilis®) used in EPDM and diisononylphthalate (DINP) used in PVC plastisols. Furthermore, the diffusion of these oils in EPDM and PVC was qualitatively determined by rheological methods. From the free volume theory of diffusion, which predicts the mutual diffusion coefficient D_{12}, we were able to study the influence of different parameters such as solubility and viscosity.

In the case of oil diffusion in EPDM at T=160°C, the polarity parameter δ_p is the first order parameter as it controls the diffusion of the oil in EPDM. δ_p must be as low as possible or at least close to the δ_p of the EPDM (δ_p = 1.9 $MP^{1/2}$). The second parameter, included in the front factor of the self-diffusion coefficient D_1, is the viscosity of the oil, which is directly related to its molar mass. As expected and due to the fact that these oils have approximately the same flow energy activation, the oil of lower viscosity will diffuse faster. Actually, the diffusion is controlled by the polar solubility parameter and the viscosity, as they are both

taken into account in the mutual diffusion coefficient. However, the polarity contribution to the solubility parameters is the first order parameter compared with the viscosity.

In the case of oil diffusion in PVC, we studied the gelation process of a plastisol. Compared with EPDM, this system is quite complex due to the nature of the PVC. From a general point of view, it can be stated that the diffusion is controlled by the solubility parameters and the viscosity of the diffusing oil, as for EPDM. However, other important parameters, such as the cohesion of the plasticised sample in the acetone test, show that the selection of a suitable molecule cannot be decided on the solubility and viscosity parameters alone.

Finally, this study shows that the solubility parameters, and more precisely the polarity parameter, are relevant in the prediction of suitable molecules for diffusion in EPDM and PVC. However, rheological experiments such as those reported in this paper are necessary to definitively select the most suitable molecules in terms of their viscosity and the final properties of the suspensions. To conclude, both of the studied methods are useful and are complementary in the design and selection of the most suitable molecules in terms of their diffusion and for practical applications.

Acknowledgements: We thank Novance and Activation for providing the base oils and the modified oils, and the Serge Ferrari and Hutchinson companies for their work on the PVC and EPDM polymers, respectively. We also thanks Elastopole and Iar for their support in the framework of the HUMEVERE project.

V- References

1. Rosen, S.L., *Fundamental principles of polymeric materials*2012.
2. Rahman, M. and C.S. Brazel, *The plasticizer market: an assessment of traditional plasticizers and research trends to meet new challenges.* Progress in Polymer Science, 2004. **29**(12): p. 1223-1248.
3. Tan, C.P. and Y.B.C. Man, *Comparative differential scanning calorimetric analysis of vegetable oils: I. Effects of heating rate variation.* Phytochemical Analysis, 2002. **13**(3): p. 129-141.
4. Lligadas, G., et al., *Renewable polymeric materials from vegetable oils: a perspective.* Materials Today, 2013. **16**(9): p. 337-343.
5. Cataldo, F., O. Ursini, and G. Angelini, *Biodiesel as a Plasticizer of a SBR-Based Tire Tread Formulation.* ISRN Polymer Science, 2013. **2013**: p. 9.
6. Petrovic, Z.S., Y.J. Xu, and W. Zhang, *POLY 395-Structure and properties of segmented polyurethanes from vegetable oil-based polyols.* Abstracts of Papers of the American Chemical Society, 2007. **234**.
7. Baltacioğlu, H. and D.m. Balköse, *Effect of zinc stearate and/or epoxidized soybean oil on gelation and thermal stability of PVC-DOP plastigels.* Journal of Applied Polymer Science, 1999. **74**(10): p. 2488-2498.
8. Shogren, R.L., et al., *Biodegradation behavior of some vegetable oil-based polymers.* Journal of Polymers and the Environment, 2004. **12**(3): p. 173-178.
9. Ronda, J.C., et al., *Vegetable oils as platform chemicals for polymer synthesis.* European Journal of Lipid Science and Technology, 2011. **113**(1): p. 46-58.
10. Li, F.K. and R.C. Larock, *Thermosetting polymers from cationic copolymerization of tung oil: Synthesis and characterization.* Journal of Applied Polymer Science, 2000. **78**(5): p. 1044-1056.
11. Wang, C.C. and F.N. Jones, *Stability and film properties of tung oil modified soybean alkyd emulsion.* Journal of Applied Polymer Science, 2000. **78**(9): p. 1698-1706.
12. Mosiewicki, M.A., et al., *Polyurethanes From Tung Oil: Polymer Characterization and Composites.* Polymer Engineering and Science, 2009. **49**(4): p. 685-692.
13. Gallezot, P., *Conversion of biomass to selected chemical products.* Chemical Society Reviews, 2012. **41**(4): p. 1538-1558.
14. Gandini, A., *Polymers from Renewable Resources: A Challenge for the Future of Macromolecular Materials.* Macromolecules, 2008. **41**(24): p. 9491-9504.
15. Choi, J.S. and W.H. Park, *Effect of biodegradable plasticizers on thermal and mechanical properties of poly(3-hydroxybutyrate).* Polymer Testing, 2004. **23**(4): p. 455-460.
16. van Oosterhout, J.T. and M. Gilbert, *Interactions between PVC and binary or ternary blends of plasticizers. Part I. PVC/plasticizer compatibility.* Polymer, 2003. **44**(26): p. 8081-8094.
17. Lepadatu, A.-M., S. Asaftei, and N. Vennemann, *Investigation of new composite materials based on activated EPDM rubber waste particles by liquid polymers.* Journal of Applied Polymer Science, 2015. **132**(25).
18. Arayapranee, W. and G.L. Rempel, *Effects of cashew nut shell liquid as a plasticizer on cure characteristics, processability, and mechanical properties of 50 : 50 NR/EPDM blends: A comparison with paraffin oil.* Journal of Applied Polymer Science, 2007. **106**(4): p. 2696-2702.
19. Duvis, T., G. Karles, and C.D. Papaspyrides, *Plasticized pvc films petroleum oils - the effect of ultraviolet-irradiation on plasticizer migration.* Journal of Applied Polymer Science, 1991. **42**(1): p. 191-198.

20. Gnanasekharan, V. and J.D. Floros, *Migration and sorption phenomena in packaged foods.* Critical Reviews in Food Science and Nutrition, 1997. **37**(6): p. 519-559.
21. Katan, L.L., *Migration phenomena in food-packaging - 3 important papers.* Plastics & Rubber International, 1979. **4**(1): p. 35-35.
22. Bocqué, M., et al., *Petro-based and bio-based plasticizers: Chemical structures to plasticizing properties.* Journal of Polymer Science Part A: Polymer Chemistry, 2016. **54**(1): p. 11-33.
23. Hildebrand, J.H. and R.L. Scott, *The solubility of nonelectrolytes*. American Chemical Society. Monograph series,no. 171950, New York: Reinhold Pub. Corp. x, 488 p.
24. J.Hildebrand and R.L. Scott, *Regular Solutions* 1962
25. Brydson, J.A., *Rubber Chemistry* 1978: Applied Science. 470.
26. Hansen, C.M., *Hansen Solubility Parameters: A User's Handbook*2007: CRC Press/Taylor & Francis Group. 544.
27. Lindvig, T., M.L. Michelsen, and G.M. Kontogeorgis, *A Flory–Huggins model based on the Hansen solubility parameters.* Fluid Phase Equilibria, 2002. **203**(1–2): p. 247-260.
28. Bicerano, J., *Prediction of polymer properties*2002: CRC Press.
29. Krevelen, D.W.V., *Properties of Polymers. Their Correlation with Chemical Structure, Their Numerical Estimation and Prediction from Additive Group Contributions*. 3rd edition ed1990: Elsevier Science Pub Co. 898.
30. Stefanis, E. and C. Panayiotou, *Prediction of Hansen solubility parameters with a new group-contribution method.* International Journal of Thermophysics, 2008. **29**(2): p. 568-585.
31. Abbott, S. and C.M. Hansen, *Hansen solubility parameters in practice*2008: Hansen-Solubility.
32. Gharagheizi, F., *New procedure to calculate the Hansen solubility parameters of polymers.* Journal of Applied Polymer Science, 2007. **103**(1): p. 31-36.
33. Archer, W.L., *Determination of Hanse solubility parameters for selected cellulose ether derivatives.* Industrial & Engineering Chemistry Research, 1991. **30**(10): p. 2292-2298.
34. Sato, T., et al., *Comparison of Hansen Solubility Parameter of Asphaltenes Extracted from Bitumen Produced in Different Geographical Regions.* Energy & Fuels, 2014. **28**(2): p. 891-897.
35. Garcia, J.C. and A. Marcilla, *Influence of the type of resin in the gelation and fusion processes of PVC plastisols.* Polymer, 1998. **39**(2): p. 431-435.
36. Joubert, C., et al., *Diffusion of plasticizer in elastomer probed by rheological analysis.* Journal of Rheology, 2002. **46**(3): p. 629-650.
37. Bella, R., et al., *Characterization and modelling of diffusion and reaction of low molecular weight reactants in molten polymer.* Polymer, 2007. **48**(23): p. 6902-6912.
38. Cassagnau, P. and F. Fenouillot, *Rheological study of mixing in molten polymers: 1-mixing of low viscous additives.* Polymer, 2004. **45**(23): p. 8019-8030.
39. Ponsard-Fillette, M., C. Barres, and P. Cassagnau, *Viscoelastic study of oil diffusion in molten PP and EPDM copolymer.* Polymer, 2005. **46**(23): p. 10256-10268.
40. Bella, R., et al., *Diffusion of liquids in molten polymers: Mutual diffusion coefficient dependence on liquid miscibility and polymer molar mass.* Polymer, 2006. **47**(14): p. 5080-5089.
41. Boudhani, H., et al., *Rheology and gelation kinetics of PVC plastisols.* Rheologica Acta, 2007. **46**(6): p. 825-838.
42. Teyssandier, F., et al., *Sol-gel transition and gelatinization kinetics of wheat starch.* Carbohydrate Polymers, 2011. **83**(2): p. 400-406.

43. Batista, M.M., R. Guirardello, and M.A. Krahenbuhl, *Determination of the Solubility Parameters of Biodiesel from Vegetable Oils.* Energy & Fuels, 2013. **27**(12): p. 7497-7509.
44. Gilbert, M., J.E. Briggs, and W. Omana, *Crystallinity in EPDM terpolymers.* British Polymer Journal, 1979. **11**(2): p. 81-88.
45. Bockisch, M., *Fats and oils handbook*1998: AOCS press.
46. Mondello, M. and G.S. Grest, *Molecular-dynamics of linear and branched alkaes.* Journal of Chemical Physics, 1995. **103**(16): p. 7156-7165.
47. Webb, E.B., G.S. Grest, and M. Mondello, *Intracrystalline diffusion of linear and branched alkanes in the zeolites TON, EUO, and MFI.* Journal of Physical Chemistry B, 1999. **103**(24): p. 4949-4959.
48. Dhoot, S.N., B.D. Freeman, and M.E. Stewart, *Sorption and transport of linear esters and branched alkanes in biaxially oriented poly(ethylene terephthalate).* Industrial & Engineering Chemistry Research, 2004. **43**(12): p. 2966-2976.

CHAPITRE II:

Publication 2: “Control of diffusion and exudation of vegetable oils in EPDM copolymers”

Control of diffusion and exudation of vegetable oils in EPDM copolymers

Cyrille Bétron, Philippe Cassagnau, Véronique Bounor-Legaré*

Univ Lyon, CNRS- UMR 5223, IMP@Lyon 1, 15 Boulevard Latarjet, F-69622 Lyon, France

Abstract

As a response to environmental problems caused by plasticisers, the feasibility of replacing a significant proportion of the plasticisers in a synthetic ethylene-propylene-diene monomer copolymer (EPDM) matrix with bio-based materials was studied. In that context, different bio-based commercials plasticisers such as Radia® supplied by Oleon, methyl soybean oil, epoxidised methyl soybean oil, methyl oleate, methyl linoleate and untreated vegetable oils (rapeseed, soybean, linseed and tung) were tested. Diffusion analysis using the bi-layers rheology method and exudation analysis highlighted an important exudation phenomenon at 80 °C for all oils tested. To overcome this problem, a second part of this work was focused on the use of a specific highly reactive vegetable tung oil. The *in situ* polymerisation of this oil by thermal activation without the use of catalysts allowed us to totally prevent the exudation phenomenon by increasing the viscosity of the oil. Compared with the use of pure tung oil, the degree of exudation was greatly decreased, from more than 8% to less than 1%.

Highlights:

- Diffusion of vegetable oils and commercial bio-based oil in EPDM matrix
- Standoil curing of tung oil
- Thermal curing of EPDM and tung oil blend to prevent exudation

Keywords: EPDM, Vegetable oils, Diffusion, Exudation, Tung oil, Standoil.

I- Introduction:

Since its introduction on the market in the early 1960s, ethylene propylene diene monomer terpolymer (EPDM) is one of the most important synthetic rubbers. EPDM exhibits excellent heat, ozone, ageing, weathering and chemical resistance being employed in a variety of applications of technical goods such as automotive profiles, building and construction, sealing and fitting systems and even as modifier for thermoplastic materials [1]. Plasticisers allow the processability of EPDM to be enhanced; the maximum amount of plasticiser incorporated into the polymer that does not exude during storage is popularly accepted as the limit of compatibility. Plasticisers can be generally classified as mineral oils, synthetic plasticisers, or vegetable oils and other natural products [2]. Mineral oils are non-polar compounds, classified by their content of aromatic, paraffinic, and naphthenic hydrocarbons. Quantities from 10 to 40 parts per hundred rubber (phr) are often used to soften the rubber and reduce its hardness as well as its elasticity modulus [3]. One major drawback of petroleum-based oils is that they are a non-renewable resource and the aromatic content of some mineral oils may render them carcinogenic [4, 5]. Replacing mineral oils with vegetable oils may be a solution to these problems. Unmodified vegetable oils have been used as plasticisers in rubber with different degrees of success [6-12]. Cashew oil was used by Arayapranee et al. [7] in small quantities (1–10 phr) in NR(natural rubber)/ EPDM mixtures. However, in their work, they reported conflicting results using this oil. Seed oil was also used in NR and styrene-butadiene rubbers (SBR) by Nandanan et al. [13] but only in low quantities (2-10 phr) due to poor compatibility with the NR rubber. Alexander et al. [6] used a cardanol at higher proportions (10–50 phr) as plasticisers for carbon black filled NR. Petrovic et al. [11] used soybean oil as a substitute for petroleum oil in NR/SBR rubber. In their work, they studied the possibility of using a cationic polymerisation of the soybean oil [14] that increased its viscosity ten-fold with respect to the untreated oil. These results show interesting possibilities for the use of polymerised soybean oil. In other studies, the oil concentration is relatively low (around 5–10 phr), which is not representative of the use of plasticisers in the elastomer industry. However, vulcanised vegetable oils or factices have a long history of use in the rubber industry. Unsaturated vegetable oils have been used for many years in the elaboration of polymeric materials. Actually, once spread out in a thin layer, some vegetable oils can dry at room temperature by an oxidative process [15, 16]. The process involves a reaction of the fatty double bonds with atmospheric dioxygen. Thus, a convenient classification has been

developed depending on the drying index, called the “iodine index,” whose value increases with the degree of unsaturation of the oil [17, 18]. This ability to naturally crosslink has been known for a very long time, in particular in the field of paint manufacture [19]. Unfortunately, the polymerisation times are very long (several days or weeks). The reaction can be accelerated by the use of thermal polymerisation, which is called the standoil reaction [20]. Oils are first heated at high temperature (>270°C) in the absence of dioxygen before polymerising by oxidation at room temperature. In this reaction fatty double bonds are thermally polymerised and TAG (triacylglyceride) molecules are crosslinked, leading to an increase in the oil viscosity with the reaction time [21]. The obtained oils are called “standoils.” Many contributions to knowledge about vegetable oil polymerisation have been reported in the last century [22-25]. Among unsaturated vegetable oils, highly reactive tung oil has been extensively applied in industry [26-31]. Tung oil-based polymers [32, 33] and tung oil as a reactive diluent [34, 35] or modifier [36] have been reported. Tung oil has also been applied as an autonomous repair agent in self-healing epoxy coatings [37], reactive diluents [38] and in UV-curable systems [39]. The tung oil derivatives was used as plasticizers for nitrile rubber for the first time by Placek *et al.* in 1960 [40]. The results obtained appeared satisfactory, the weight loss was been between 0.5 and 2% after aged 48h at 100°C for the tung oil derivatives and the hydrogenated tung oil derivatives. All of these studies show the strong interest of the scientific community in this highly reactive vegetable oil in many fields, with the additional aim of finding "green alternatives" to the use of petroleum resources.

In this work, we first studied the plasticiser power of vegetable oils or commercial bio-based oils in an EPDM copolymer. The aim was to simply screen the suitable molecules in terms of their final applications in plasticised EPDM. In the second part of the study, an approach based on the standoil phenomenon was developed to prevent oil exudation. The high reactivity of the tung oil was exploited for its polymerisation at a temperature of around 250°C under an inert atmosphere (standoil process).

II- Experimental

II-1) Materials and reagents

- ***EPDM matrix***

The EPDM used is a Vistalon® 8600 (ExxonMobil Chemical) kindly supplied by Hutchinson. The structural formula was defined by ^{1}H NMR analysis (Fig. 1). The average molar mass values M_n= 69,000 g/mol and M_w= 203,000 g/mol were measured by size exclusion chromatography. Its density is 870kg/m^3 and its Mooney Viscosity ML (1+8 at 125°C) is 81MU based on test ASTM D1646. The solubility parameters obtained by chemical method [41] are δ_D=18.29MPa$^{1/2}$, δ_P=1.91 MPa$^{1/2}$, and δ_H=2.03 MPa$^{1/2}$ resulting in a global solubility parameter δ_{tot}=18.5 MPa$^{1/2}$ and a radius of interaction of 7.2.

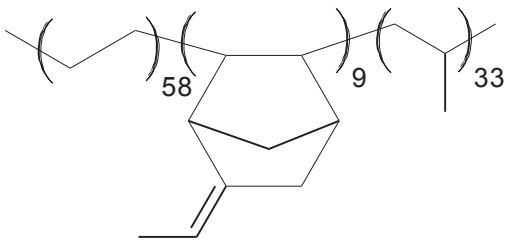


Fig. 1. EPDM Vistalon® 8600 structural formula with the mass percent of each repeat unit

- ***Mineral and vegetable oils***

A mineral oil (Torilis® 7200, TotalFina-Elf, France) was used as a reference for oil plasticiser into the Vistalon 8600 to mimic industrial compositions. The specific gravity of this oil is 0.90 g cm^{-3} at 20 °C.

A selection of vegetable and industrial oils was used. The commercial Radia® oils were supplied by the Oleon Company, the mineral oil by the Hutchinson Company and the vegetable oils were ordered from Sigma-Aldrich and Oleon. The fatty acid composition of the vegetable oils was defined by ^{1}H NMR (for example, see the ^{1}H NMR spectrum of the tung oil in Fig. 2). All vegetable oils were analysed using the same methods and the results are in agreement with those found in the literature [42-49].

Table 1. Description of industrial oils

Industrial oils	Composition/ main components
Torilis® 7200	Mineral oil
Radia® 7331	2-ethylhexyl oleate
Radia® 7129	2-ethylhexyl palmitate
MeSBO	Methyl ester of soybean oil
MeESBO	Epoxidized methyl ester of soybean oil
MeOleate	Methyl Oleate
MeLinoleate	Methyl Linoleate

Table 2. Fatty acid components of vegetable oils.

Vegetable oils	Saturated fatty acids %wt	α-eleostearic 18:3 %wt	Linolenic acid 18:3 %wt	Linoleic acid 18:2 %wt	Oleic acid 18:1 %wt
Rapeseed oil	6.9	0.0	10.5	20.3	62.3
Soybean oil	24.8	0.0	6.9	49.3	21.2
Linseed oil	8.3	0.0	53.4	16.1	22.2
Tung oil	5.6	80.9	0.0	9.2	4.3

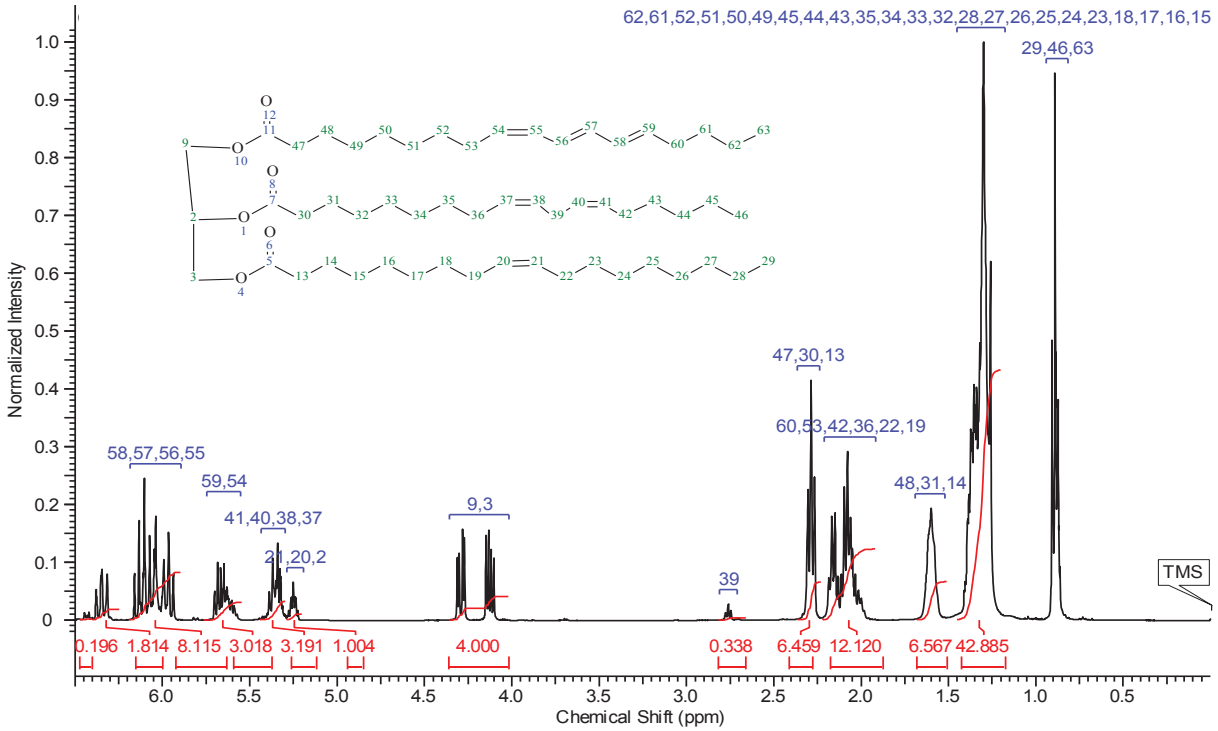


Fig. 2. Liquid ^{1}H NMR spectrum of tung oil (Toluene d8, at 30°C)

II-2) Sample preparation

The EPDM samples were prepared in an internal batch mixer (Haake Rheomix 50 cm^3), at a rotor speed of 50 rpm and a temperature of 160°C. The following protocol was adopted: First, the polymer was introduced into the chamber and is mixed for 5 min in order to ensure the thermal homogeneity. At the end of the mixing process, all samples were compression moulded into 1 mm-thick sheets at 160 °C for 10 min and at 130 °C for 5 hours to reduce the stress relaxation phenomenon. Samples of 50 mm diameter were used to study the diffusion efficiency by the bi-layers method studied in work of Bella R, Cassagnau P, *et al.* [50, 51]. In addition, to study the miscibility of the oil in EPDM, an EPDM sample (disk of 25 mm diameter and 1 mm thick) was totally immersed in the plasticiser at room temperature. This sample was then weighed at different time points during seven days of immersion.

To study the plasticisation effect in terms of viscoelastic behaviour (G*(ω)), the EPDM and 30 % of plasticiser by weight were introduced into an internal batch mixer at 80 rpm and 160°C. After mixing, the sample was prepared by compression moulding at 180 °C for 5 min in a form of a disk of 25 mm diameter and 1mm thickness.

II-3) Methods of characterisation

- ***Rheology characterisation***

A specific protocol based on the bi-layer principle was followed for diffusion experiments, using an ARES 4800 instrument. This method has already been used in a previous work [41] to compare the chemical influence of different oils on their diffusion in a EPDM matrix. The polymer disk was placed on the lower plate in the heated oven and allowing it to melt or its shape to relax in order to obtain a plane surface. The plasticiser was inserted between the polymer sample and the upper plate using a syringe. The air gap was adjusted to allow 20% by weight of the plasticiser to be injected. The variation of the dynamic modulus G' and G'' and of the complex viscosity η* during diffusion of the oil into the polymer matrix was followed by time sweep oscillatory shear experiments (ω= 10 $rad.s^{-1}$). Furthermore, a frequency sweep oscillatory shear experiment ($0.01<\omega$ ($rad.s^{-1}$)<100) was performed at the same temperature at the end of the diffusion process.

- ***Swelling and solubility test***

Swelling and solubility experiments were carried out by immersing a sample in a suitable solvent. The system was allowed to reach equilibrium, and the amount of solvent absorbed by the sample was measured using gravimetric methods.

For the swelling experiments, the sample was then rinsed and dried. The un-crosslinked polymer chains were extracted and the sample mass measured [52-54]. The insoluble mass and the swelling rate are defined to determine the cross-linking density using the equation:

$$Q = {}^{V_s}/_{V_i} \quad (1)$$

where Q is the coefficient of swelling, V_s the swelling volume and V_i is the initial volume before the swelling experiment. This equation can be described by:

$$Q = (m_s/d_s + m_p/d_p)/(m_p/d_p) \quad (2)$$

where m_s is the mass of solvent in the swelling polymer and $d_s = 867\text{kg.m}^{-3}$, the density of toluene used in the present case, m_p the mass of swelling polymer and $d_p = 933\text{kg.m}^{-3}$ the density of the polymer, in this case the polymerised tung oil.

- ***Exudation test***

To check the exudation phenomenon, a sample of EPDM was mixed until full incorporation with 30% by weight of oil. The sample mass was measured, and then placed in an oven at 80 °C for 7 days (a standard test in the industry). The sample was then wiped with absorbent paper to remove excess oil from the surface, and the weighed again. The mass difference between before and after heating allowed us to define the oil loss by exudation [55, 56].

- ***DSC analysis***

The DSC analysis was carried out using a DSC Q200 TA instrument coupled with liquid nitrogen as a cooling medium. The DSC instrument was calibrated with indium. A tung oil or EPDM/oil sample was loaded into a standard aluminium pan and the cover was hermetically sealed using the manufacturer's crimping tool. An empty and hermetically sealed aluminium pan was used as reference. Firstly, the tung oil sample was heated to 30 °C and held for 5 min at this temperature. The sample was then cooled from 30 °C to −150 °C at 5

°C/min and held at this temperature for 3 min. The sample was then heated again from −150 °C to 150 °C at 5 °C/min and the melting peaks were recorded.

- ***Liquid ^{1}H NMR spectroscopy***

The liquid ^{1}H NMR spectra were measured on a Bruker 400 Avance III (5mm) instrument with a BBFO+ probe at a frequency of 400 MHz at 30 °C. 30 mg of sample were solubilised in 1 ml of Toluene d8 and TMS was used as a reference.

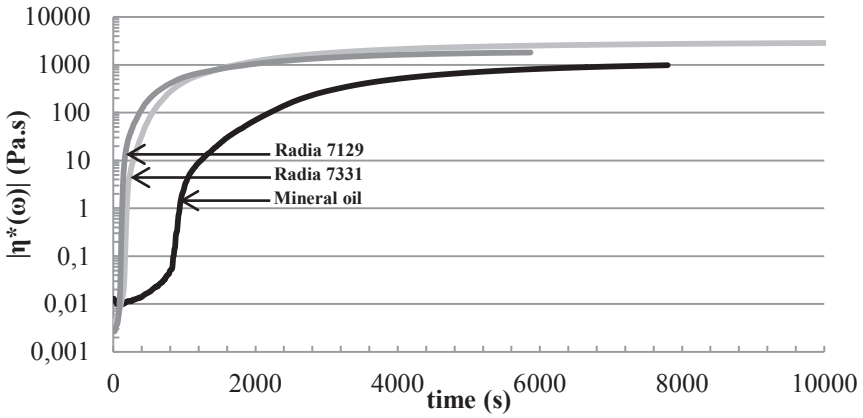
III- Results and discussion

III-1) Plasticisation of EPDM by oils

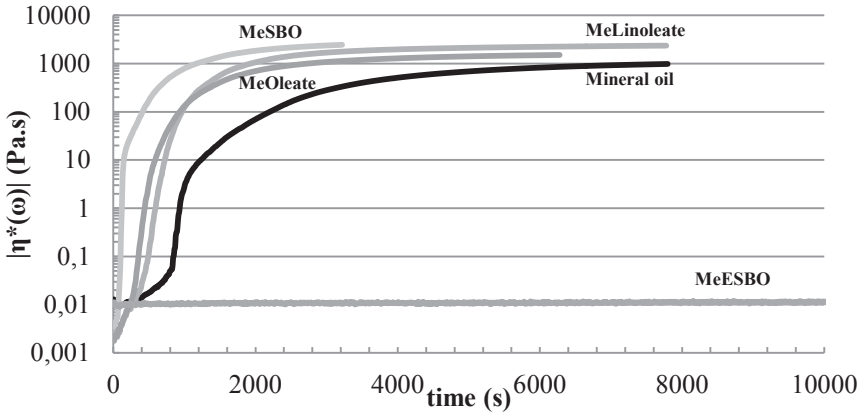
- ***Oil diffusion***

As explained in the experimental section, the bi-layers method was used to determine the diffusion ability of plasticiser oils in the molten polymer. Fig. 3 shows the rheological diffusion curves of a few commercial oils (Radia® oils), and methyl and fatty ester oils in EPDM.

a)



b)



c)

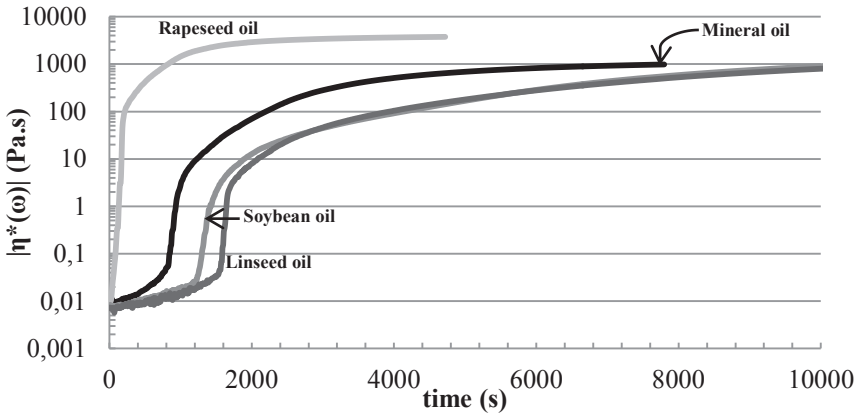


Fig. 3. Variation of the absolute complex viscosity |η*(ω)| versus time (ω=10 rad s-1) at 160°C in EPDM matrix by bi-layers method for different oils. a) Commercial oils (Radia), b) methyl ester oils, c) fatty oils. The mineral oil is used as reference.

In Fig. 3a, we compare the diffusion of the mineral oil (reference) with the Radia commercial oils based on fatty acid methyl esters (FAME). In Fig. 3b we study the diffusion of methyl FA (fatty acid) and epoxy methyl FA. Finally, Fig. 3c shows the diffusion of the un-modified vegetable oils. From these diffusion curves, two populations of oils can be identified with regards to their diffusion ability in EPDM. The most significant are the MeESBO, for which the $|\eta^*(\omega)|$ value stays at around 10^{-2} Pa.s during the test, evidencing no diffusion. As discussed in our previous study [41] a value equal or greater than 10^3 Pa.s for the absolute complex viscosity means total solubility of the oil with EPDM. We observed that below this value the sample is not homogenous and a portion of the plasticiser did not diffuse. The diffusion is due to a chemical affinity that can be defined by the Hansen solubility parameters calculated in earlier work [41]. For the EPDM matrix, the low polar contribution of the plasticiser, δ_p=1.91 $MPa^{1/2}$, is a good indicator of the miscibility between the EPDM and the plasticiser. Plasticisers with a high polar contribution, for example those containing the epoxy functional group (MeESBO with δp=5.5 $MPa^{1/2}$) or other polar functional groups result in lower coefficients of diffusion. This rheological test can be used as an indicator to rapidly screen the oil diffusion in the molten polymer, using low quantities of the product (around 1.2 mL). From these curves it can be qualitatively concluded that Radia and the rapeseed oils diffuse faster than soybean and linseed oils.

- ***Oil plasticising efficiency***

The plasticising efficiency of the oils was studied at 160 °C using an EPDM formulation with 30% by weight of plasticiser, as commonly used in rubber formulations by the Hutchinson Company (Fig. 4). In all cases and as expected, a decrease of the modulus was observed compared to pure EPDM.

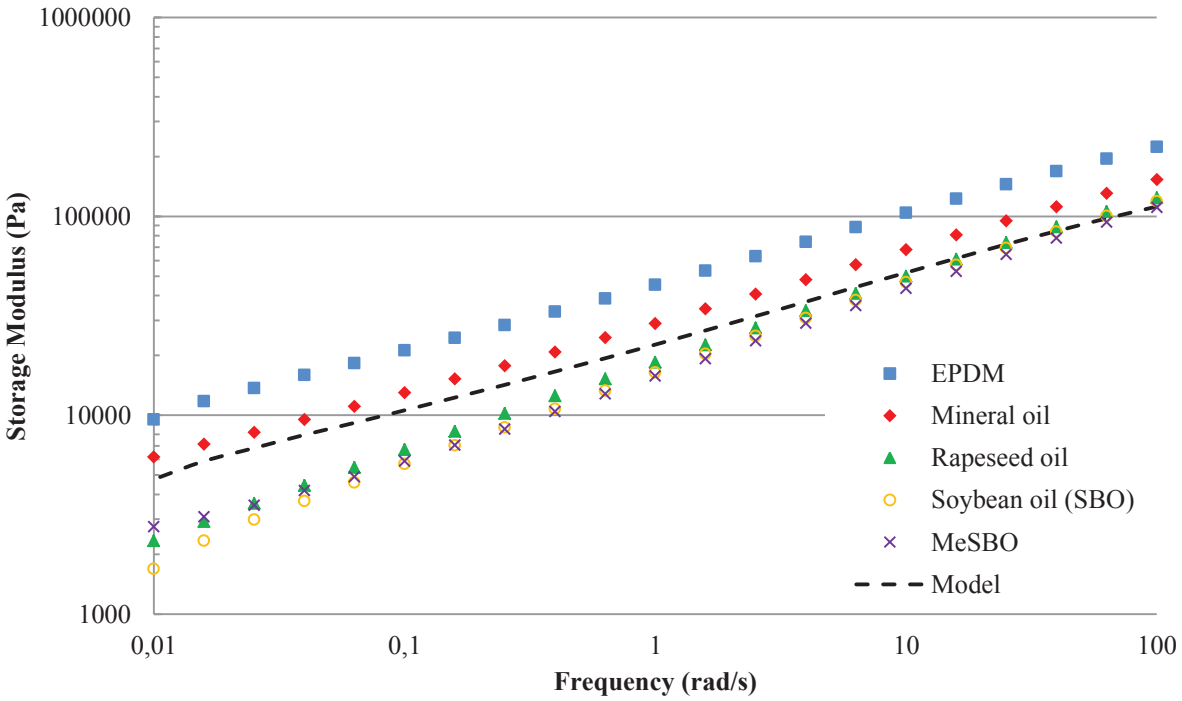


Fig. 4. Variation of the storage modulus G' versus frequency at 160°C for EPDM samples plasticized with 30%w of different oils.

The effect of plasticiser oils on the EDPM matrix has been previously studied by Ponsard-Fillette et al. [57] using the variation of the complex shear modulus. Furthermore, they refer to a theoretical framework of the dilution effect which was discussed in detail by Marin et al. [58] and extended by Gimenez et al. [59]. The viscoelastic parameters such as the plateau modulus can then be expressed

$$G^0_{N_{solution}} = G^0_{N_{bulk}} \phi^{2.25} \quad (3)$$

with ϕ the polymer volume fraction and G^0_N. Due to the elastic behaviour of the EPDM (G′>>G″ throughout the frequency range) the Eq (3) can be extended to the storage modulus i.e.:

$$G'_{(\omega)_{solution}} = G'_{(\omega)_{bulk}} \phi^{2.25} \quad (4)$$

This model of the plasticising effect is shown in Fig. 4. It demonstrates that the model predicts the storage modulus of the EPDM/Mineral oil systems quite well. However the model underestimates the plasticising effect of the vegetable oils, which are better than the mineral oil in this experiment. This result means that there is better disentanglement of

polymer chains by the vegetable oils than by the mineral oil. Paradoxically, this rheological behaviour evidences a better plasticising efficiency of the vegetable oils compared with the theoretical model, even though they presented lower solubility in the EPDM matrix.

- ***Oil exudation***

To complete the experiments concerning diffusion and plasticising power, the exudation phenomenon was studied at room temperature. This information is crucial for material applications. A good plasticiser must be miscible with the matrix at room temperature to prevent exudation problems. The results of the solubility experiments, as described in the experimental section, are reported in Table 3.

Table 3. Uptake (solubility) and loss (exudation) weight of vegetables oils in EPDM at 20°C

Plasticizer	%wt uptake	%wt loss
Mineral oil	Soluble	1.1
Radia® 7331	Soluble	15.6
Radia® 7129	Soluble	16.3
MeSBO	Soluble	17.4
MeOleate	Soluble	16.9
MeLinoleate	63.2	17.1
Linseed oil	18.6	12.8
Rapeseed oil	16.1	15.8
Soybean oil	12.4	27.2
Tung oil	11.9	8.4
MeESBO	0.1	Ø

Plasticisers such as mineral oils are able to completely dissolve in the EPDM matrix. However the results are quite different for the vegetable oils. To be considered as a good plasticiser in terms of processing, the oil uptake must be at least 30–40% by weight. Based on this standard, commercial oils such as Radia (Radia® 7331 and Radia® 7129), the methyl soybean oil (MeSBO), MeOleate and the MeLinoleate can be considered as good plasticisers of the EPDM matrix. These results confirm the paradox that good diffusion at 160 °C is not a good indication of solubility. For example, rapeseed oil has poor solubility with an uptake value of 16.1% by weight but diffuses quickly in the matrix as shown in Fig. 3. Regarding the

non-modified vegetable oils, their solubility is relatively poor as their uptake does not exceed 20% and consequently these oils could not be used in industrial EPDM applications.

Regarding the exudation properties, the weight losses from the different oils are reported in Table 3. The results show a significant exudation phenomenon for all oils except for the mineral oils. Oils with a low molar mass such as MeSBO have a high rate of diffusion in the EPDM matrix and could be considered as a good choice of plasticiser. Unfortunately, these low molar mass oils also display the most exudation. The oils with the most favourable diffusion rates are actually the most prone to exudation. For the vegetable oils the results are more variable. While the exudation is extensive for the soybean oil, we observed that it was less prominent for more unsaturated oils such as linseed oil or tung oil. In view of these results, plasticising of the EPDM matrix by modified oils does not appear to be effective. In fact the low molar mass (i.e. low viscosity) that appears to be an advantage in terms of the diffusion and mixing processes appears to be a drawback in terms of exudation from the final material. A previous study [41] highlighted that the differences between the Torilis 7200 and vegetable oils are due to their different activation energies. The mineral oil has a high flow activation energy of E_a= 73 kJ.mol^{-1} and the viscosity of 4.0x10^{-2} Pa.s at 160 °C increases to a viscosity of 1.60 Pa.s at 20 °C. Meanwhile, the vegetable oils have low flow activation energy ($E_a \approx$ 25 kJ.mol^{-1}) and the viscosity of 2x10^{-2} Pa.s at 160 °C increases to a viscosity in the range 3x10^{-2} to 9x10^{-2} Pa.s at 20 °C. Consequently, mineral and vegetable oils which have nearly the same viscosity at the processing temperature (T=160 °C) have a quite different viscosity at room temperature, the viscosity of the mineral oil being approximately ten times higher than the viscosity of the vegetable oils at this temperature.

Consequently, as we cannot significantly increase the viscosity of the vegetable oils by decreasing the temperature, one solution is to increase the molar mass of the vegetable oil during mixing and processing. Therefore, our next objective was to take advantage of the oil thermal reactivity during its incorporation into the polymer matrix during processing. This method allowed us to increase the molar mass of the vegetable oil and therefore to prevent the exudation phenomenon. For that purpose, we wanted to select a vegetable oil with a very high reactivity, and we therefore naturally focused on tung oil.

III-2) Plasticisation of EPDM by tung oil

- ***Expected reaction***

At high temperatures around 300–350°C, two main reactions can be observed with the very reactive tung oil as shown in Fig. 5 and Fig. 6: a Diel-Alder addition and free radical reactions on the unsaturated function of the vegetable oil [60, 61]. In the first case, the thermal energy allows a double bond rearrangement of the polyunsaturated fatty acids into a conjugated system. This first step is necessary for the success of the second step, which involves a reaction between the diene moiety of a triacylglyceride (TAG) molecule and one double bond of a second TAG molecule. In such a diene addition, one of the conjugated systems acts as the diene, while a double bond from another molecule acts as the dienophile. The product of the Diels-Alder addition reaction is a cyclic unsaturated structure as described in Fig. 5. For the tung oil, 80% by weight of the conjugated tri-unsaturated bonds (α-eleostearic acid**)** are prone to this reaction, which can explain its high reactivity.

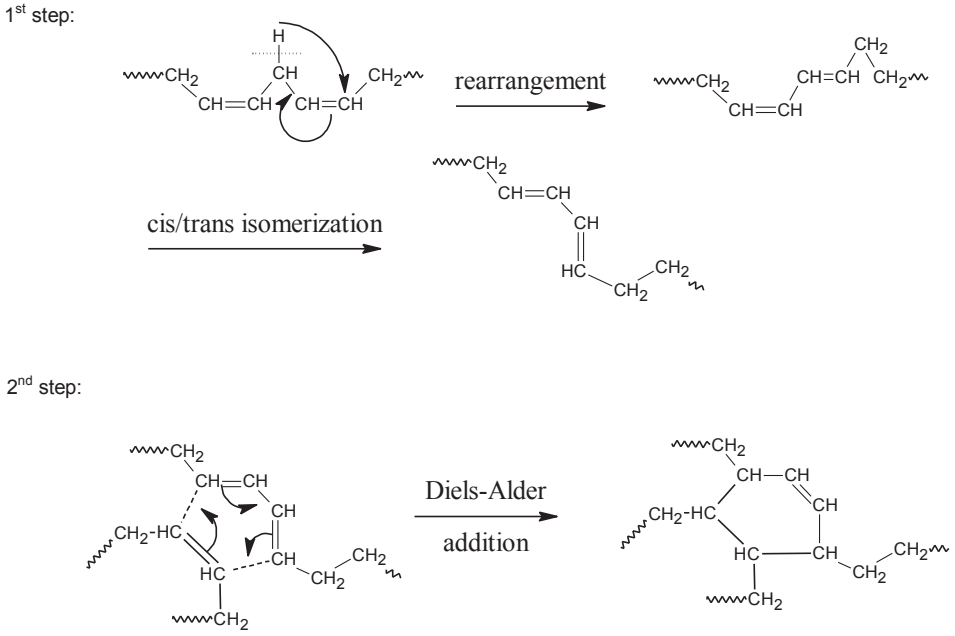


Fig. 5. Tung oil rearrangement and Diels-Alder reactions [60]

Another reaction which corresponds to hydrogen abstraction from the carbon located between two non-conjugated double bonds is described in another study [62]. It is associated with radical additions with recombination steps, and lead to dimers and trimers as shown in

Fig. 6. According to the methylene radical delocalisation or to the double bond environment, addition products with conjugated double bonds can also be obtained.

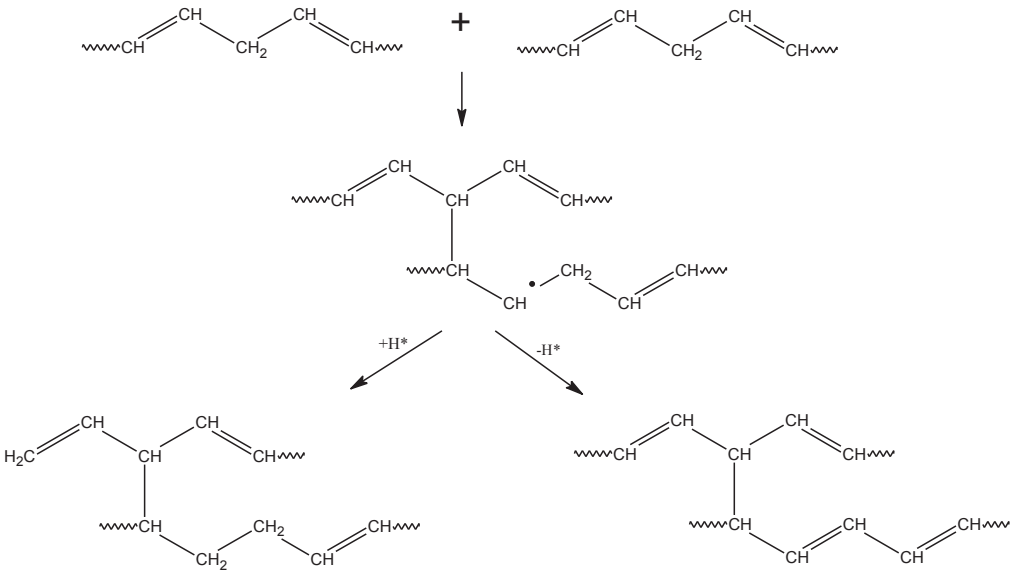


Fig. 6. Radical reaction of tung oil at high temperature [60]

- ***Polymerisation of the tung oil***

Intra-molecular polymerisation, also called standoil reaction, of the tung oil leads to a significant modification of the absolute complex viscosity as shown in Fig 7.

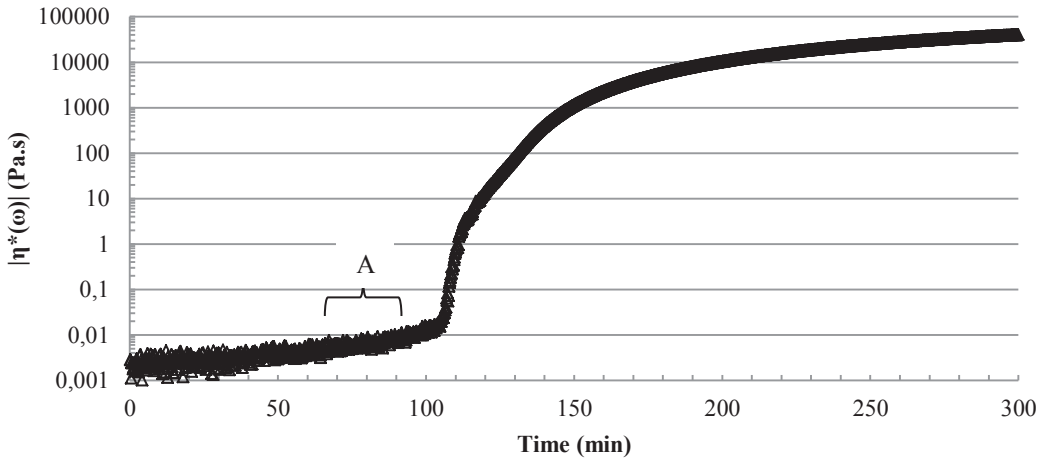


Fig. 7. Variation of the absolute complex viscosity versus time (ω=6.283 rad s^{-1}) for the standoil reaction of pure tung oil (220°C)

Analysis of the variation of the complex viscosity versus time shows a typical crosslinking curve. This homopolymerisation is composed of three different steps as described in the standoil section. To confirm these hypotheses and the formation of a network, the material obtained at the end of the previous experiment and cured for 300 min at 220 °C was immersed in toluene for swelling analysis. The insoluble fraction, close to 95% by weight, evidences the efficiency of the crosslinking reaction. The swelling ratio of 2.7 confirms the creation of a 3D network. Therefore, these results confirmed the possibility of drastically increasing the viscosity and the molar mass of tung oil by curing at high temperature. From the variation of the complex shear modulus (crossover of G′ and G″ modulus, not shown here) the gelation time is observed at t=106 min. bearing in mind that the objective of the present study is only to increase the oil viscosity (part of the area A in Fig. 7) in order to prevent the exudation phenomenon, this reaction is in a suitable time range compatible with the EPDM processing (10–20 min) at 250 °C. Thus, this approach appears to be a suitable approach to prevent the exudation phenomenon by *in situ* curing of the Tung oil after its diffusion into the elastomer.

After full incorporation of 30% by weight of Tung oil into the EPDM matrix at 250°C, the torque and temperature were monitored versus time as shown in Fig. 8.

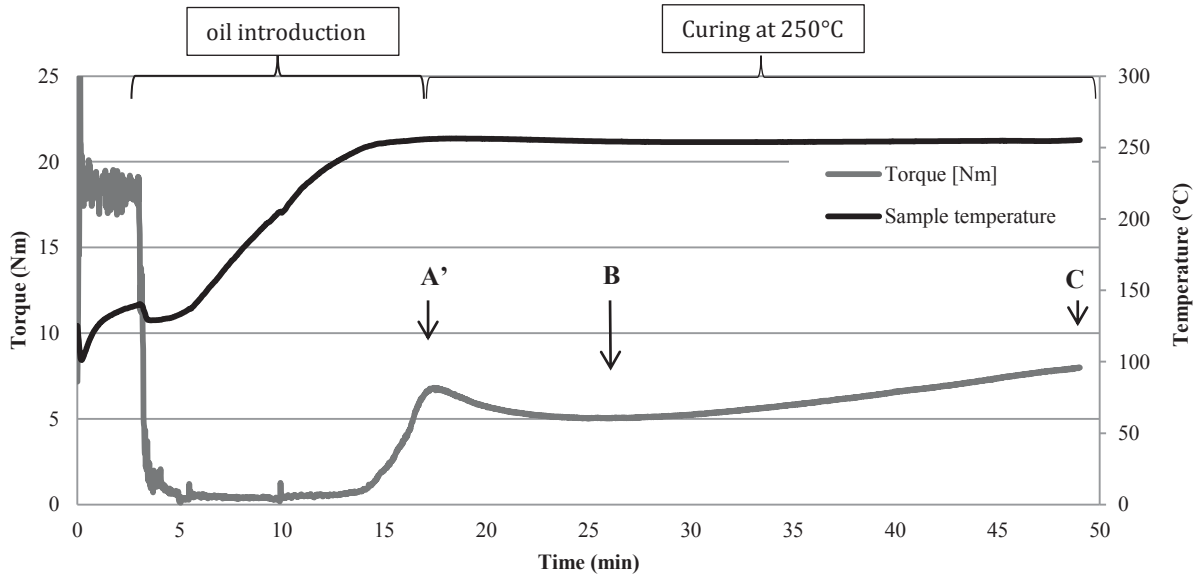


Fig. 8. Variation of the torque and temperature versus mixing time for the EPDM/tung oil (70/30wt%).

At first, the torque, which can be related to the viscosity of the molten media, decreases drastically with the oil incorporation at 140 °C (lubricant effect). After 10-15 minutes of mixing, the torque increases due to the diffusion and mixing of the oil into the EPDM, which forms a homogeneous media (Zone A' in Fig. 8). The slight decrease in the torque between the points A' and B is due to the homogenisation of the medium. Finally the torque slightly increases with the mixing time due to the polymerisation of the Tung oil. Furthermore, no insoluble fraction was observed showing that this mixing/curing process does not change the EPDM polymer structure. As the polymerised Tung oil is not crosslinked, we only observe an increase of the viscosity of reacted oil chains.

Further analysis was performed on this sample (Fig. 8, point C) by liquid ^{1}H NMR. The spectrum was compared to the one obtained with the non-cured compound (Fig. 8, point (A')). We focused on signals in the range 5 to 7ppm, which corresponds to the proton resonance of mono, di and tri unsaturated fatty acids. From the intensity ratio, we estimated that approximately 50mol % of triene (signal at 6.5ppm) had reacted. At 6.30 ppm corresponding to the proton resonance of di-unsaturated fatty acids, we observed a 30% decrease in signal intensity. Finally, a 10 % decrease in the intensity of the signals at 5.3 ppm, corresponding both to the norbornene double bond and to mono unsaturated bonds from tung oil, was observed.

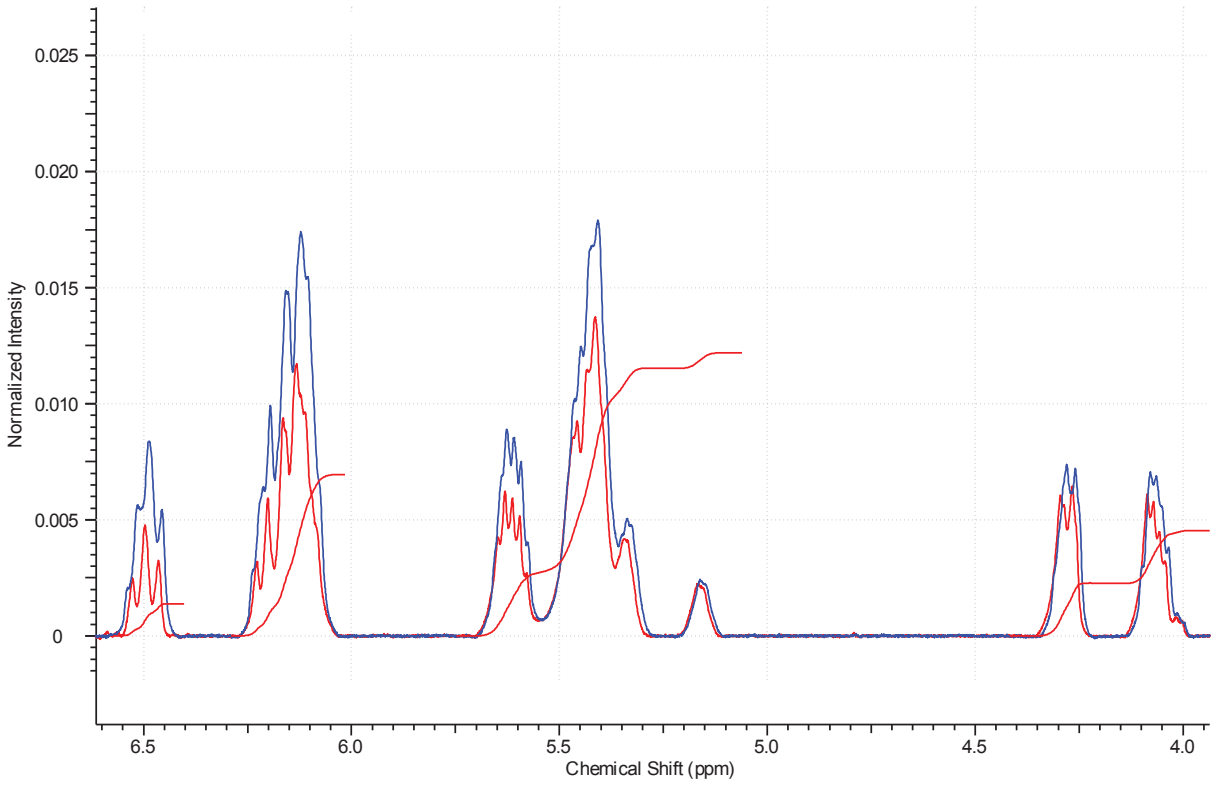


Fig. 9. Liquid ^{1}H NMR spectra of EPDM blend with 30%wt of tung oil. Upper spectrum before curing (A') and lower spectrum after curing at 250°C (C). (toluene d8 at 30°C)

From these data, it is not possible to determine which is the main reaction (Diels-Alder or free radical reaction) responsible for the decrease in the concentration of unsaturated bonds. However the superposition of the signal at 5.1 ppm corresponding to unsaturated norbornene proton resonance may indicate that the EPDM matrix is not affected by this curing reaction, which is also in agreement with the previous results for the insoluble fraction.

Finally, the impact of the standoil reaction on several properties was investigated. First, the viscoelastic behaviour of the previous EPDM based material was analysed and compared with that obtained with non-plasticised EPDM, EPDM plasticised with 30 wt% of mineral oil and EPDM plasticised with 30wt% of tung oil without curing (Fig. 10). The storage modulus G' is significantly affected by this curing treatment. With a thermal treatment at 250 °C for 25 min, the values of the storage modulus for the cured tung oil-based EPDM blend are higher than those for the non-cured tung oil. This result emphasises that the chemical modification of the vegetable oil by homopolymerisation decreases the disentanglement ability of the vegetable oil compared to the non-cured tung oil. It is therefore important to limit the Tung oil curing time to avoid a complete loss of its ability to disentangle EPDM chains. Nevertheless, it is interesting to note that the rheological behaviour of the cured tung oil-based material and the mineral oil based one are very similar even if this result is fortuitous.

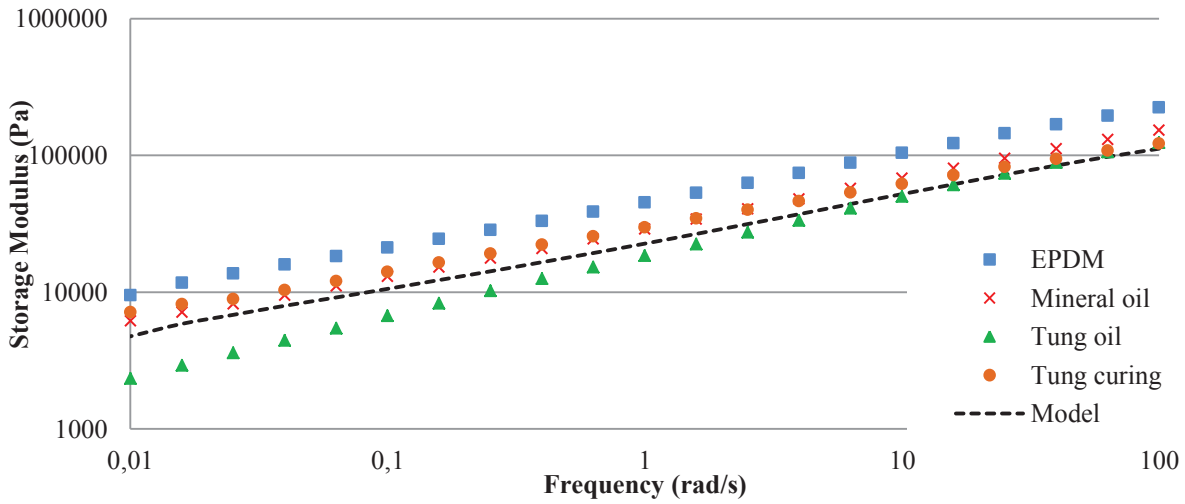


Fig. 10. Variation of the storage modulus G' versus frequency (rad/s) for the pure EPDM and EPDM plasticized with 30%w of different oils at 160°C.

Variations in the thermal transitions of EPDM/Tung oil and EPDM/standoil were evaluated with regards to the final temperature range of their application [63]. In the literature, tung oil presents a melting point of around 0–7 °C [64]. However, Ward *et al.* [65] explain in this work that one component of the alpha form of the oil began melting at approximately -43°C, and at -10°C the rate of solid to liquid-phase transformation increased. But most of the oil seemed to be melted at 3°C although some crystals persisted possibly until 37°C. In our thermal analysis (Fig. 11) we observed a melting temperature of -6.15 °C this confirms results. Between -80 °C and -40 °C, we noticed successive melting and recrystallisation phenomena due to imperfect crystal formation during the cooling period. We noted a crystallisation temperature at -22.3°C. After curing the tung oil for a few minutes at 260 °C, it could be observed than the crystallisation point and the melting point had disappeared. The chemical modifications caused by the standoil reactions led to the formation of a network that prevents recrystallisation of the tung oil while preserving its plasticising properties. Consequently, this method allows us to prevent the crystallisation of the tung oil, which increases the temperature range of its applications.

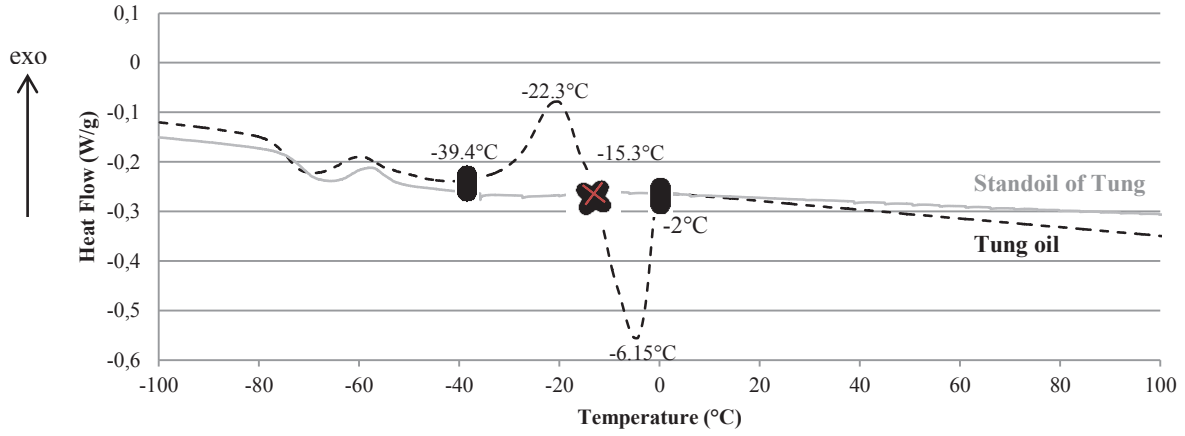


Fig. 11. Comparative thermograms of pure and cured tung oil (few minutes at 260°C)

The same analysis was carried out with plasticised EPDM, as shown in Fig. 12.

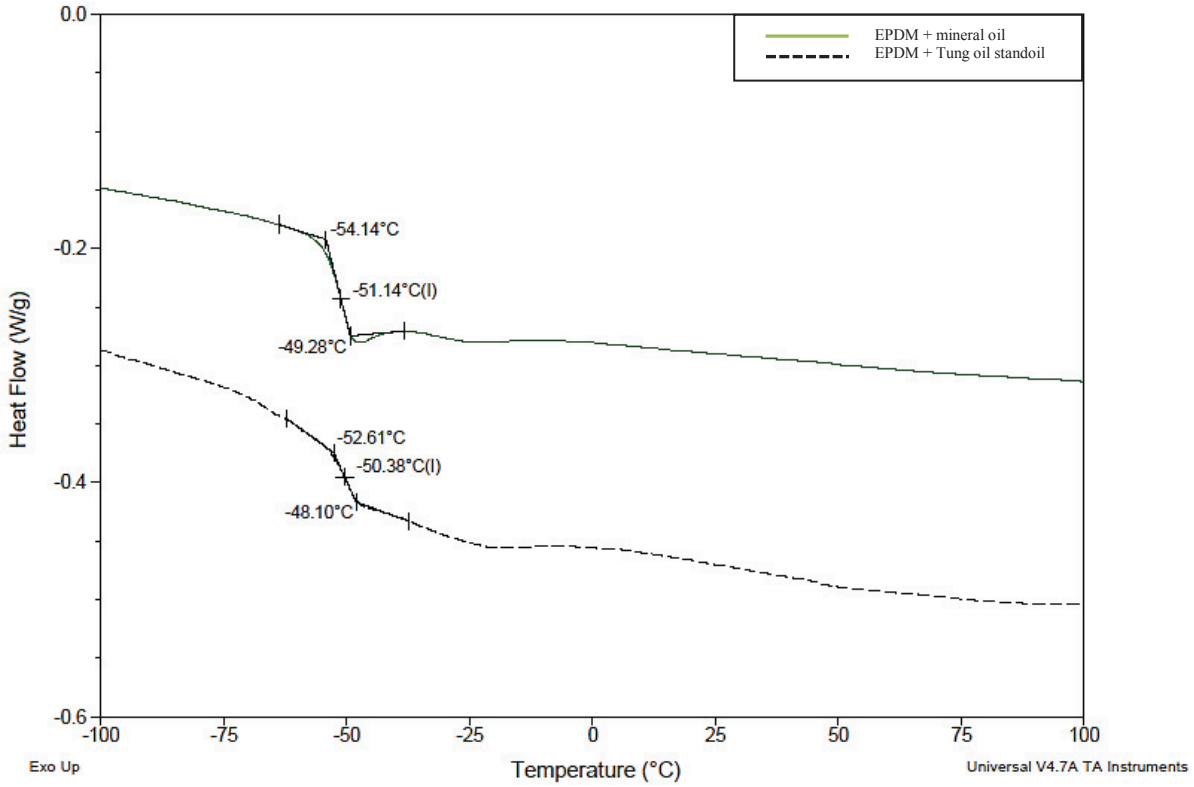


Fig. 12. Thermal properties of EPDM/30wt% mineral oil and EPDM/30wt% tung oil after curing under mixing (point C on curve Fig. 8).

The results showed that both samples undergo a similar thermal transition associated with the T_g (T_g -50°C). No other thermal transition is observed such as the crystallisation or melting seen with tung oil.

The most important reason for the use of the standoil reaction was to eliminate exudation from the EPDM. The weight loss at 80 °C for different EPDM/30 wt% oil blends was evaluated in comparison with the reference based on mineral oil (Table 4).

Table 4. Weight loss (%) for EPDM/30wt% oils based samples after 7 days at 80°C.

Plasticizer	**% weight loss**
Soybean oil (SBO)	27.2
Tung oil	8.4
Tung Standoil	0.8
Mineral oil	1.1

Analysis of these results showed that the standoil reaction had a real effect on the exudation phenomenon. Compared with the use of pure tung oil, the exudation was greatly decreased, from more than 8% down to less than 1%. This last value is thus close to that obtained with EPDM plasticised with mineral oil. This approach is therefore a very interesting alternative to the use of mineral oil, based on a highly reactive vegetable oil that is able to react under the EPDM processing conditions and achieve final properties close to the reference.

IV- Conclusion

In this study, several vegetable oils were tested in terms of their efficiency of plasticising EPDM. A mineral oil, extensively used in the industry, was used as reference. The diffusion at T=160 °C of these oils in the EPDM was probed by a two-layer rheological experiment. It can be qualitatively concluded that commercial vegetable oils (Radia: 2-ethylhexyl oleate 2-ethylhexyl palmitate) and rapeseed oils diffuse faster than soybean and linseed oils. However, a strong exudation phenomenon of these oils at T=80 °C was observed. Compared with mineral oil, this exudation is a major drawback for the development of these oils in EPDM material applications. To understand this phenomenon and to propose an alternative, tung oil was used which is an unsaturated and reactive fatty acid vegetable oil. The *in situ* polymerisation of this oil by thermal activation allowed us to totally prevent the exudation phenomenon by increasing the viscosity. To make this technology competitive it is now necessary to find other applications besides use as a plasticiser, for example as a fire retardant or in crosslinking reactions.

Acknowledgments:

We thank Novance and Activation for providing the vegetable oils and the Hutchinson company for their work on EPDM processing. We also thank Evea for life cycle analysis of different oils, the poles of competitiveness Techtera, Elastopole and IAR for their support and finally the HUMEVERE project.

V- References

1. Lepadatu, A.-M., S. Asaftei, and N. Vennemann, *Investigation of new composite materials based on activated EPDM rubber waste particles by liquid polymers.* Journal of Applied Polymer Science, 2015. **132**(25).
2. Bocqué, M., et al., *Petro-based and bio-based plasticizers: Chemical structures to plasticizing properties.* Journal of Polymer Science Part A: Polymer Chemistry, 2016. **54**(1): p. 11-33.
3. Wypych, G., *11 - Plasticizers use and selection for specific polymers*, in *Handbook of Plasticizers (Second Edition)*, G. Wypych, Editor 2012, William Andrew Publishing: Boston. p. 307-419.
4. Cruickshank, C.N.D. and J.R. Squire, *Skin cancer in the engineering industry from the use of mineral oil.* British Journal of Industrial Medicine, 1950. **7**(1): p. 1-11.
5. Roy, T.A., et al., *Correlation of mutagenic and dermal carcinogenic activities of mineral-oils with polycyclic aromatic compound content.* Fundamental and Applied Toxicology, 1988. **10**(3): p. 466-476.
6. Alexander, M. and E.T. Thachil, *A comparative study of cardanol and aromatic oil as plasticizers for carbon-black-filled natural rubber.* Journal of Applied Polymer Science, 2006. **102**(5): p. 4835-4841.
7. Arayapranee, W. and G.L. Rempel, *Effects of cashew nut shell liquid as a plasticizer on cure characteristics, processability, and mechanical properties of 50 : 50 NR/EPDM blends: A comparison with paraffin oil.* Journal of Applied Polymer Science, 2007. **106**(4): p. 2696-2702.
8. Labauze, G. and D. Vasseur, *Rubber composition for a tire tread*, 2007, US Patent 7253225.
9. Nandanan, V., R. Joseph, and D.J. Francis, *Linseed oil as a multipurpose ingredient in NBR vulcanizate.* Journal of Elastomers and Plastics, 1996. **28**(4): p. 326-334.
10. Perrone, R.J., *Polychloroprene plasticized with corn oil*, 1980, US Patent 4220574.
11. Petrovic, Z.S., et al., *Soybean oil plasticizers as replacement of petroleum oil in rubber.* Rubber Chemistry and Technology, 2013. **86**(2): p. 233-249.
12. Cataldo, F., O. Ursini, and G. Angelini, *Biodiesel as a Plasticizer of a SBR-Based Tire Tread Formulation.* ISRN Polymer Science, 2013. **2013**: p. 9.
13. Nandanan, V., R. Joseph, and K.E. George, *Rubber seed oil: A multipurpose additive in NR and SBR compounds.* Journal of Applied Polymer Science, 1999. **72**(4): p. 487-492.
14. Ionescu, M. and Z.S. Petrovic, *Cationic polymerization of biological oils with superacid catalysts*, 2009, US Patent 7501479.
15. Oyman, Z.O., W. Ming, and R. van der Linde, *Oxidation of model compound emulsions for alkyd paints under the influence of cobalt drier.* Progress in Organic Coatings, 2003. **48**(1): p. 80-91.
16. van Gorkum, R. and E. Bouwman, *The oxidative drying of alkyd paint catalysed by metal complexes.* Coordination Chemistry Reviews, 2005. **249**(17-18): p. 1709-1728.
17. Wicks Jr, Z.W., et al., *Organic coatings: science and technology*. Third Edition ed2007: Wiley. 746.
18. Wold, C.R. and M.D. Soucek, *Mixed metal oxide inorganic/organic coatings.* Journal of Coatings Technology, 1998. **70**(882): p. 43-51.
19. Clocker, E.T., *Condensation product and method*, 1940, US Patent 2188882.
20. Sigwalt, P., *La polymerisation thermique des huiles siccatives a doubles liaisons non conjuguees.* Bulletin De La Societe Chimique De France, 1955(11-1): p. 1643-1650.

21. Fountain, C.W., et al., *Viscosity of common seed and vegetable oils.* Journal of Chemical Education, 1997. **74**(2): p. 224-227.
22. Croston, C.B., et al., *Polymerization of drying oils .6. catalytic polymerization of fatty acids and esters with boron trifluoride and hydrogen fluoride.* Journal of the American Oil Chemists Society, 1952. **29**(8): p. 331-333.
23. Pestemer, M. and J. Tschinkel, *Untersuchung der Standölbildung durch Lichtabsorptionsmessung im Ultraviolett.* Fette und Seifen, 1943. **50**(3): p. 153-158.
24. Cowan, J.C., et al., *Polymerization of drying oils - rubberlike products from polymeric fat acids.* Industrial and Engineering Chemistry, 1949. **41**(8): p. 1647-1653.
25. Maschke, A. and A. Mendl, *Investigation by means of ultraviolet spectroscopy of the catalytic bodying of linseed oil (comparison with the uncatalyzed process).* Journal of Polymer Science, 1950. **5**(4): p. 429-442.
26. Huang, Y., G. Ye, and J. Yang, *Synthesis and properties of UV-curable acrylate functionalized tung oil based resins via Diels–Alder reaction.* Progress in Organic Coatings, 2015. **78**(0): p. 28-34.
27. Yang, X., et al., *Novel renewable resource-based UV-curable copolymers derived from myrcene and tung oil: Preparation, characterization and properties.* Industrial Crops and Products, 2015. **63**(0): p. 17-25.
28. Liu, C., et al., *Use of tung oil as a reactive toughening agent in dicyclopentadiene-terminated unsaturated polyester resins.* Industrial Crops and Products, 2013. **49**(0): p. 412-418.
29. Meiorin, C., M.A. Mosiewicki, and M.I. Aranguren, *Ageing of thermosets based on tung oil/styrene/divinylbenzene.* Polymer Testing, 2013. **32**(2): p. 249-255.
30. Huang, Y., et al., *Synthesis and properties of UV-curable tung oil based resins via modification of Diels–Alder reaction, nonisocyanate polyurethane and acrylates.* Progress in Organic Coatings, 2013. **76**(4): p. 654-661.
31. Sharma, V. and P.P. Kundu, *Addition polymers from natural oils—A review.* Progress in Polymer Science, 2006. **31**(11): p. 983-1008.
32. Bhuyan, S., et al., *Effect of crosslinking on tribological behavior of tung oil-based polymers.* Tribology International, 2010. **43**(4): p. 831-837.
33. Meiorin, C., M.I. Aranguren, and M.A. Mosiewicki, *Polymeric networks based on tung oil: Reaction and modification with green oil monomers.* European Polymer Journal, 2015. **67**: p. 551-560.
34. Biermann, U., et al., *Esters of calendula oil and tung oil as reactive diluents for alkyd resins.* European Journal of Lipid Science and Technology, 2010. **112**(1): p. 103-109.
35. Nalawade, P.P., et al., *Modified Soybean Oil as a Reactive Diluent: Synthesis and Characterization.* Journal of Polymer Science Part A: Polymer Chemistry, 2014. **52**(21): p. 3045-3059.
36. Pereda, M., M.I. Aranguren, and N.E. Marcovich, *Caseinate films modified with tung oil.* Food Hydrocolloids, 2010. **24**(8): p. 800-808.
37. Samadzadeh, M., et al., *Tung oil: An autonomous repairing agent for self-healing epoxy coatings.* Progress in Organic Coatings, 2011. **70**(4): p. 383-387.
38. Thanamongkollit, N., K.R. Miller, and M.D. Soucek, *Synthesis of UV-curable tung oil and UV-curable tung oil based alkyd.* Progress in Organic Coatings, 2012. **73**(4): p. 425-434.
39. Wutticharoenwong, K., J. Dziczkowski, and M.D. Soucek, *Tung based reactive diluents for alkyd systems: Film properties.* Progress in Organic Coatings, 2012. **73**(4): p. 283-290.
40. Placek, L.L., et al., *Tung oil derivatives as plasticizers for buna-N rubber.* Journal of the American Oil Chemists Society, 1960. **37**(6): p. 307-309.

41. Bétron, C., et al., *Diffusion of modified vegetables oils in thermoplastic polymers.* submit, 2016.
42. Cahoon, E.B., et al., *Biosynthetic origin of conjugated double bonds: Production of fatty acid components of high-value drying oils in transgenic soybean embryos.* Proceedings of the National Academy of Sciences of the United States of America, 1999. **96**(22): p. 12935-12940.
43. Park, J.Y., et al., *Production and characterization of biodiesel from tung oil.* Applied Biochemistry and Biotechnology, 2008. **148**(1-3): p. 109-117.
44. Agriculture, U.S.D.o. *USDA National Nutrient Database for Standard Reference*. 07/12/2011 [cited 2015 01/06]; Available from: http://ndb.nal.usda.gov//.
45. Ma, F. and M.A. Hanna, *Biodiesel production: a review1.* Bioresource Technology, 1999. **70**(1): p. 1-15.
46. Bockisch, M., *Fats and oils handbook*1998: AOCS press.
47. Goering, C., et al., *Fuel properties of eleven vegetable oils.* ASAE Tech. Pap.;(United States), 1982. **25**(6).
48. Radunz, A., P. Heb, and G. Schmid, *Analysis of the seed lipids of Aleurites montana.* Zeitschrift für Naturforschung C, 1998. **53**(5-6): p. 305-310.
49. Ramos, M.J., et al., *Influence of fatty acid composition of raw materials on biodiesel properties.* Bioresource Technology, 2009. **100**(1): p. 261-268.
50. Bella, R., et al., *Diffusion of liquids in molten polymers: Mutual diffusion coefficient dependence on liquid miscibility and polymer molar mass.* Polymer, 2006. **47**(14): p. 5080-5089.
51. Bella, R., et al., *Characterization and modelling of diffusion and reaction of low molecular weight reactants in molten polymer.* Polymer, 2007. **48**(23): p. 6902-6912.
52. Neuburger, N.A. and B.E. Eichinger, *Critical experimental test of the Flory-Rehner theory of swelling.* Macromolecules, 1988. **21**(10): p. 3060-3070.
53. Chi, M.S., *Compatibility of cross-linked polymers with plasticizers by glass-transition temperature-measurement and swelling tests.* J. Polym. Sci. Part A: Polym. Chem, 1981. **19**(7): p. 1767-1779.
54. Flory, P.J., *Statistical mechanics of swelling of network structures.* Journal of Chemical Physics, 1950. **18**(1): p. 108-111.
55. Chen, J., et al., *Synthesis and application of a natural plasticizer based on cardanol for poly(vinyl chloride).* Journal of Applied Polymer Science, 2015. **132**(35): p. n/a-n/a.
56. Altenhofen da Silva, M., et al., *Polyvinylchloride (PVC) and natural rubber films plasticized with a natural polymeric plasticizer obtained through polyesterification of rice fatty acid.* Polymer Testing, 2011. **30**(5): p. 478-484.
57. Ponsard-Fillette, M., C. Barres, and P. Cassagnau, *Viscoelastic study of oil diffusion in molten PP and EPDM copolymer.* Polymer, 2005. **46**(23): p. 10256-10268.
58. Marin, G., et al., *Propriétés viscoélastiques linéaires de solutions de polybutadiène en régime semi-dilué et concentré.* Rheologica Acta, 1980. **19**(4): p. 462-476.
59. Gimenez, J., P. Cassagnau, and A. Michel, *Bulk polymerization of epsilon-caprolactone: Rheological predictive laws.* Journal of Rheology, 2000. **44**(3): p. 527-547.
60. Zovi, O., et al., *Stand reaction of linseed oil.* European Journal of Lipid Science and Technology, 2011. **113**(5): p. 616-626.
61. Cowan, J.C., et al., *Polymerization of Drying Oils.* Industrial and Engineering Chemistry, 1949. **41**(8): p. 1647-1653.

62. Rushman, D.F. and E.M.G. Simpson, *The thermal polymerization of methyl linoleate. Part 1.-The uncatalyzed reaction.* Transactions of the Faraday Society, 1955. **51**(0): p. 230-236.
63. Tan, C.P. and Y.B.C. Man, *Comparative differential scanning calorimetric analysis of vegetable oils: I. Effects of heating rate variation.* Phytochemical Analysis, 2002. **13**(3): p. 129-141.
64. Gunstone, F.D., J.L. Harwood, and F.B. Padley, *The Lipid Handbook, Second Edition*1994: Taylor & Francis.
65. Ward, T.L., W.S. Singleton, and R.W. Planck, *Thermal properties of fats and oils. VIII. Specific heats, heats of fusion, and entropy of alpha and beta tung oils.* Journal of the American Oil Chemists Society, 1952. **29**(4): p. 155-157.

CHAPITRE III:

Publication 3: “EPDM crosslinking from bio-based vegetable oil and Diels-Alder reactions”

EPDM crosslinking from bio-based vegetable oil and Diels–Alder reactions

Cyrille Bétron, Véronique Bounor-Legaré, Philippe Cassagnau

CNRS, UMR5223, Ingénierie des Matériaux Polymères, Université Lyon 1, 15, Bd. Latarjet, F-69622 Villeurbanne, cedex, France

Abstract

The aim of this work is to study and develop a green process of plasticization and crosslinking of an EPDM matrix with a thiofuran coupling agent. For this purpose, tung oil, composed of around 80 wt% of α-eleostearic acid, was used as both a plasticizer and a thermal crosslinker. Owing to the low compatibility and weak interactions between vegetable oils and the EPDM matrix, we used in this work a di-functional compatibilizing agent derived from the food industry, 2-furanmethanethiol. The 2-furanmethanethiol was successfully grafted by a thiol–ene reaction onto both the tung oil and the EPDM matrix. The formulation was thermally treated by a continuous process in order to crosslink the EPDM matrix and the tung oil by the expected Diels–Alder reaction. The grafting was analyzed by liquid ^{1}H NMR spectroscopy. The crosslinked sample was characterized by different mechanical tests. The sample was also compared with an EPDM sample crosslinked by dicumyl peroxide (DCP) and plasticized by mineral oil.

Keywords: EPDM, tung oil, standoil, homopolymerization, thiol-ene, 2-furanmethanethiol.

I- Introduction

In recent years, several studies have been carried out on the substitution of petro-based plasticizers by biodegradable ones in order to solve the problems generated by plastic waste. In general, rubber compounds are cross-linked by sulfur vulcanization [1-3] or peroxide curing [4], and sometimes with an alternative specific system such as resol curing [5]. Sulfur vulcanization is the most popular method. It makes variable crosslink types, including mono-, di-, and polysulfides [6-9], and leads to the formation of longer or shorter sulfide links. Peroxides are also used for the crosslinking of elastomers, the main ones being dibenzoyl peroxides, and dialkyl, aryl–alkyl, peroxy–ketal and peroxy esters. This type of radical crosslinking leads to the creation of very stable covalent C-C single bonds by reaction with the C=C double bonds [10, 11]. It is also known that the nature of the crosslinking reaction, i.e., its chemical type and density, determines the physical properties of the resulting vulcanized rubber [12-16]. By increasing the crosslinking density, the Young modulus, hardness, resilience and abrasion resistance increase, whereas the elongation at break, heat buildup and stress relaxation decrease.

Of course, there are many other techniques for crosslinking a polymer matrix, for example by poly-condensation, acid-base reaction, etc., but also by using the thiol–ene reaction. The thiol–ene reaction is performed under mild reaction conditions, giving high conversion and selectivity. In addition, no toxic metal catalysts are needed, making the use of thiol–ene chemistry suitable for an eco-friendly polymer modification widely applicable to synthetic polymers [17-19]. Equally, matrix films having ene functionalities have been synthesized using the thiol–ene click addition and by alkoxysilane [20, 21], esterification and etherification chemistry [22, 23]. The most common use of thiol–ene chemistry is for the formation of crosslinked networks [24-30]. This concept has now been extended from bulk materials to hydrogels, thin films, and lithographic applications, where a wide variety of novel studies have recently been reported [31-38]. For example, utilizing thiol–ene click photochemistry, Kusuma et al. [39] synthesized films comprising poly(ethylene oxide) and polysiloxane. In addition, the reaction of pentenoic acid esters of hyaluronic acid and dextran with different thiols under UV light has been reported [40]. The thiol–ene reaction is among the most attractive and best known in chemistry, and its flexibility and versatility make it very useful in many fields [41].

Alternatively, the Diels–Alder reaction generally provides simple, efficient, and clean procedures to generate new bonds by inter- or intramolecular coupling, and represents one of

the most useful synthetic methods in organic chemistry [42, 43]. In this [4 + 2] reaction, a dienophile is typically added to a conjugated diene to give a cyclic product, called an adduct. The furan ring is one of the most common heterocycles used as the diene in Diels–Alder reactions [44]. The interest in exploiting the Diels–Alder reaction in the context of furan chemistry is motivated by the renewable character of these heterocyclic compounds (furfural is an industrial commodity obtained from a wide variety of agricultural residues). Moreover, the pronounced dienic nature of the furan ring makes it particularly suitable in terms of reaction kinetics and yields [45, 46]. The Diels–Alder reaction has also been employed as a useful technique to induce the crosslinking of various polymer structures by inter-macromolecular coupling with a di-functional complementary reagent, or polymers bearing maleimide moieties and di-furans, for example [47-50]. The advantages of this reaction are the creation of C-C bonds that are stable over time and the possibility of sequencing the reaction with the thiol–ene reaction by thermal control.

In order to substitute the conventional EPDM crosslinking agents, 2-furanmethanethiol (FFM) has been used as a new crosslinker in the present work. Note that this molecule is generally used as a flavoring agent, particularly in chocolate, fruits, nuts and coffee [51]. As the EPDM matrix is unable to react with the furan function, we circumvented this issue by using a vegetable oil as a plasticizer able to react with the furan function in order to crosslink the EPDM. In fact, in a previous work [52], we studied the heat treatment of a vegetable oil in an EPDM matrix in order to prevent the phenomenon of exudation. The present work will take advantage of this reactivity: the FFM will be used to covalently link the vegetable oil (tung oil) with the elastomer matrix to create a bio-based crosslinking network. Finally, in this work, thiol–ene chemistry will then be coupled with the Diels–Alder reaction by sequencing the reactions.

II- Experimental

II-1) Materials and reagents

The EPDM used was a Vistalon® 8600 (ExxonMobilChemical). Its chemical structure was determined by liquid ^{1}H NMR spectroscopy (Fig. 1). At 7.0 ppm we observed a signal corresponding to the proton resonance of aromatic groups due to the presence of oil. The Vistalon functionality corresponds to 0.74 mmol of diene per gram of EPDM. The average molar mass values, M_n = 69,000 g·mol^{-1} and M_w = 203,000 g·mol^{-1}, were measured by size exclusion chromatography. Its density is ρ = 870 kg·m^{-3} and its Mooney viscosity ML (1+8 at

125°C) is 81 MU based on test ASTM D1646. The solubility parameters are δ_D = 18.29 $MPa^{1/2}$, δ_P = 1.91 $MPa^{1/2}$, δ_H = 2.03 $MPa^{1/2}$ for a global solubility parameter δ_{tot} = 18.5 $MPa^{1/2}$. This material was kindly supplied by Hutchinson.

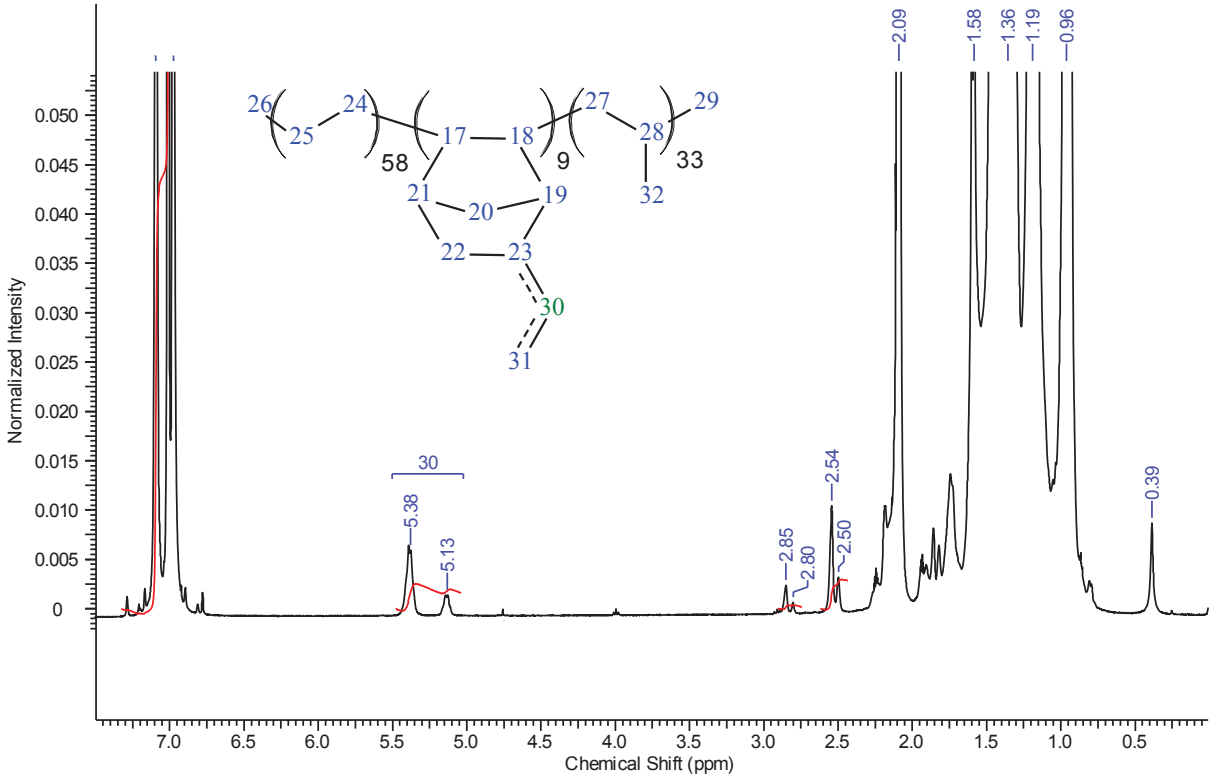


Fig. 1. Liquid ^{1}H NMR spectrum of EPDM Vistalon® 8600 (toluene d-8 at 30 °C)

The FFM supplied by Sigma-Aldrich was analyzed by liquid ^{1}H NMR (Fig. 2). Its boiling temperature is 155°C, with a molar mass of 114.17 $g \cdot mol^{-1}$ and a density of 1.132 $g \cdot mL^{-1}$ at 25°C.

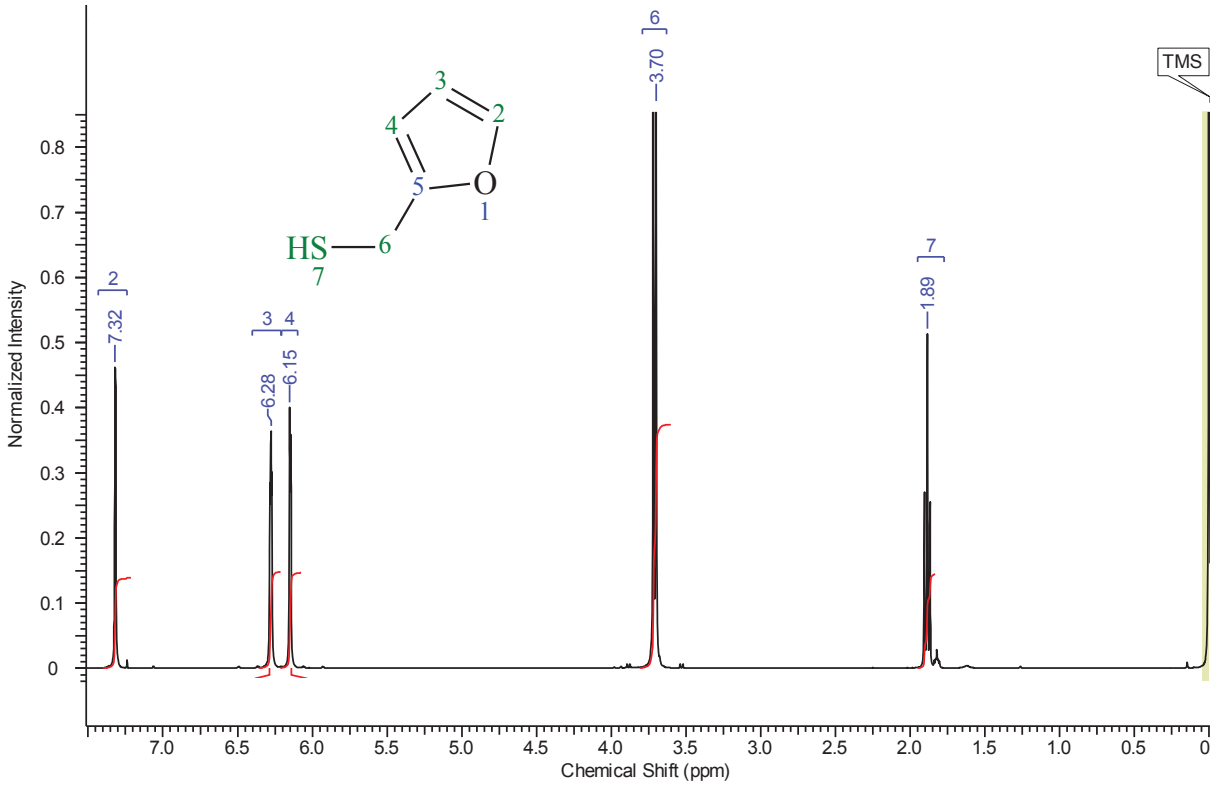


Fig. 2. Liquid ^{1}H NMR spectrum of 2-furanmethanethiol (toluene d-8 at 30°C)

Difurfuryldisulfide (DiFFM) with a purity of 95% supplied by Sigma-Aldrich was analyzed by liquid ^{1}H NMR (Fig. 3). We observed the presence of around 25 mol% of the FFM component. It has a boiling temperature of 230°C with a molar mass of 226.32 g·mol^{-1} and a density of 1.233 g·mL^{-1} at 25°C.

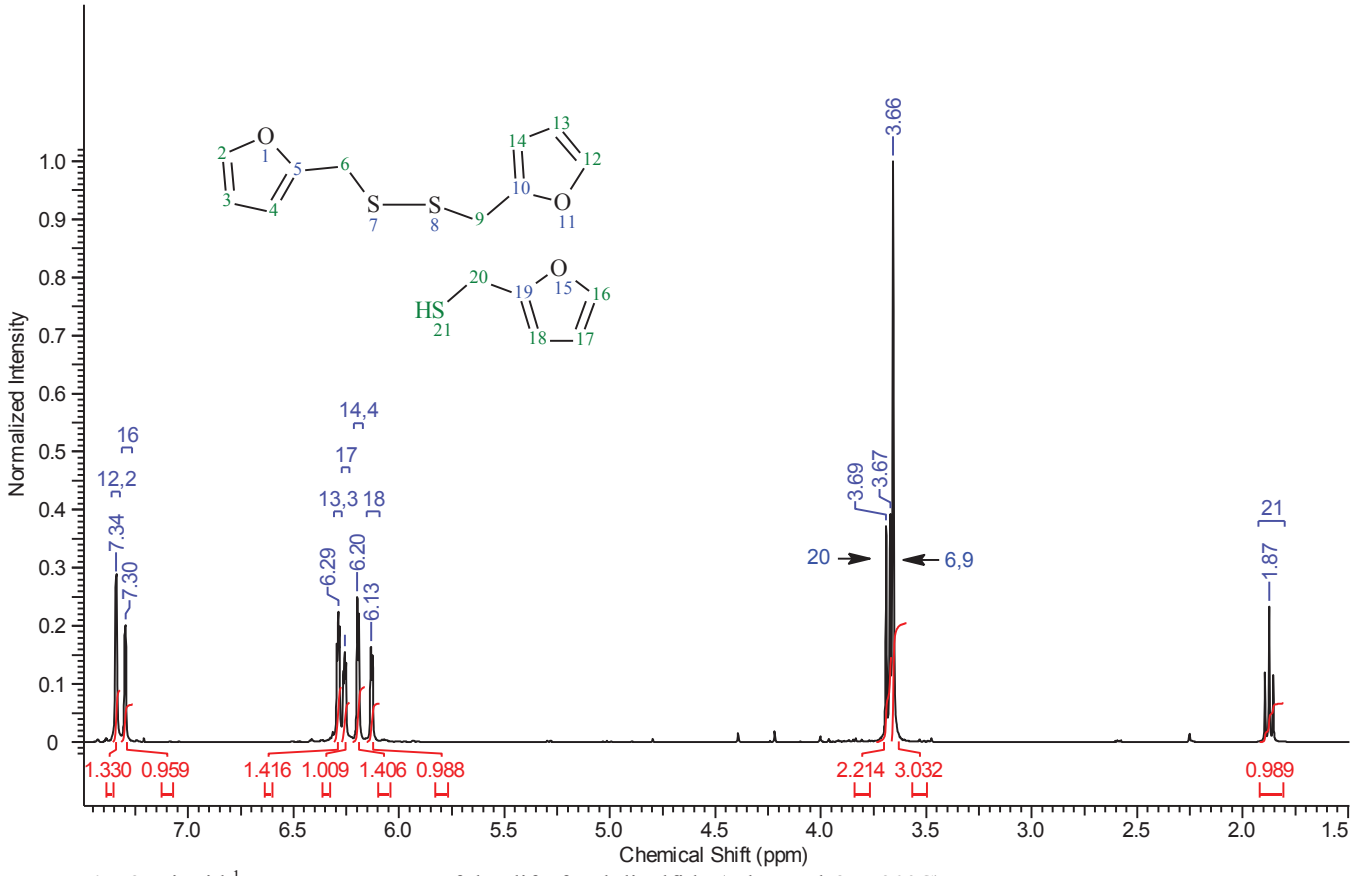


Fig. 3. Liquid ^{1}H NMR spectrum of the difurfuryl disulfide (toluene d-8 at 30°C).

Two oils were used in this study. The first one was Torilis® 7200, used as a reference. The specific gravity of this oil is 0.90 g·cm^{-3} at 20°C. The solubility parameters are δ_D = 19.8 MPa$^{1/2}$, δ_P = 0.8 MPa$^{1/2}$, δ_H = 5.0 MPa$^{1/2}$ for a global solubility parameter δ_{tot} = 20.5 MPa$^{1/2}$. It is a commercial mineral oil commonly used for EPDM plasticization. The second one is tung oil supplied by Sigma-Aldrich. This is a vegetable oil used as a very reactive plasticizer. Its chemical structure was determined by ^{1}H NMR (Fig. 4). The specific gravity of this oil is 0.937 g·cm^{-3} at 20°C. The solubility parameters are δ_D = 16.7 MPa$^{1/2}$, δ_P = 5.7 MPa$^{1/2}$, δ_H = 5.8 MPa$^{1/2}$ for a global solubility parameter δ_{tot}=18.5 MPa$^{1/2}$.

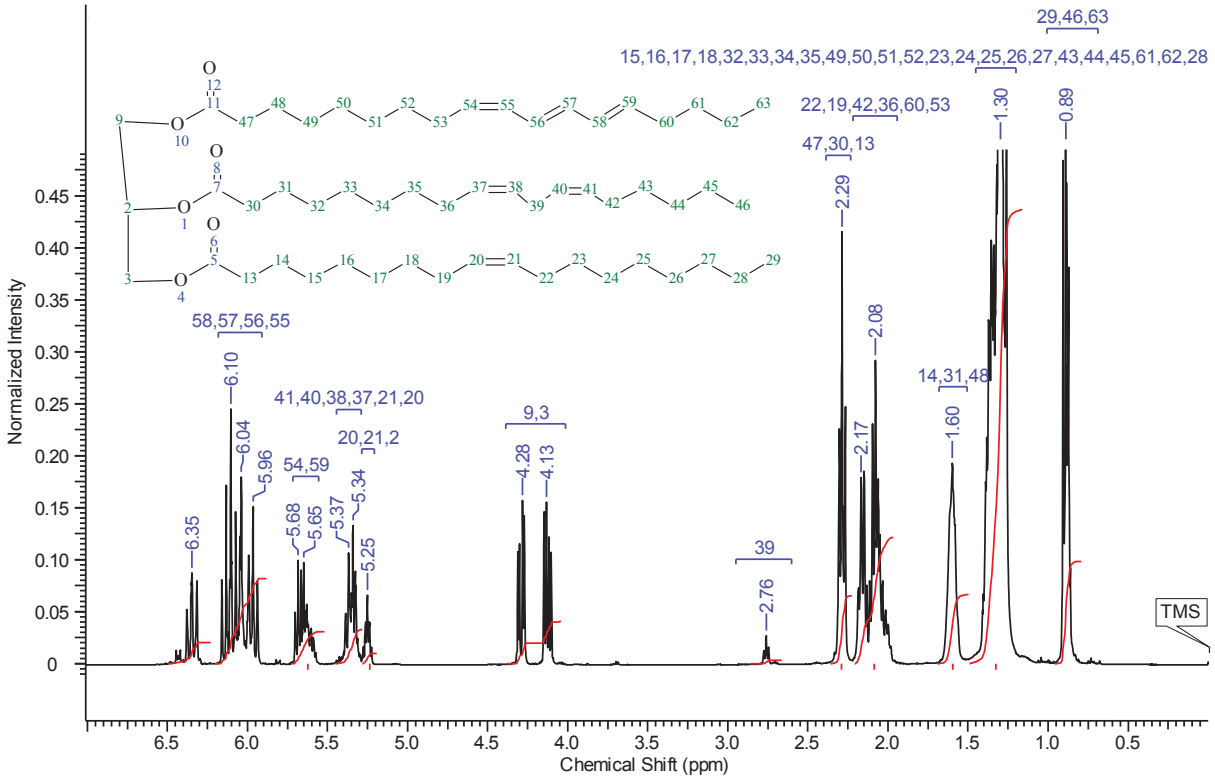


Fig. 4. Liquid ^{1}H NMR spectrum of Tung oil (toluene d-8 at 30°C).

Finally, dicumyl peroxide (DCP) with a purity of 98% was supplied by Sigma-Aldrich and was used to crosslink an EPDM sample used as a reference for comparison.

II-2) Sample preparation

- ***Static EPDM crosslinking by 2-furanmethanethiol and peroxide***

The EPDM samples crosslinked by DCP were prepared in an internal batch mixer (Haake Rheomix 50 cm^3), at 50 rpm and at a temperature of 80°C to avoid activating radical reactions during mixing. The following protocol was adopted: First, 30 g of EPDM (22.2 mmol of diene) and 0.5 wt% (0.9 mmol) or 1 wt% (1.8 mmol) of crosslinking agents were introduced into the cavity and mixed for 5 min in order to ensure thermal homogenization. In the second step, 30 wt% of Torilis® 7200 plasticizer was introduced and mixed until complete homogenization. Then, all samples were compression-molded into 1 mm-thick sheets at 180°C for 10 min to activate the DCP decomposition and the crosslinking reactions.

The EPDM samples crosslinked with the FFM molecule were prepared using the same method. 3 mL of FFM (29.7 mmol), corresponding to a molar ratio of 1.3/1 of thiol relative to the EPDM diene functions, was mixed with the EPDM for 10 min at 140°C. The amount of FFM was chosen to obtain a slight excess of thiol functions compared with the norbornene

functions. Then, in the second step, 30 wt% of tung oil (142.5 mmol of unsaturated groups) was introduced and mixed until complete homogenization. Finally, all samples were compression-molded into 1 mm-thick sheets at 250°C and cured for different times to evaluate the crosslinking reaction efficiency.

- ***Dynamic EPDM crosslinking by FFM and DiFFM***

The EPDM samples were prepared in the internal batch mixer, at 50 rpm and at a temperature of 140°C. The protocol of mixing was the same as the previous one. However, the temperature was gradually increased up to 260°C during mixing and after the addition of tung oil. With these conditions the dynamic curing treatment time was 20 min.

II-3) Methods of characterization

- ***Liquid ^{1}H NMR***

The liquid ^{1}H NMR spectra were measured on Bruker 400 Avance III (5 mm) with BBFO+ probe at a frequency of 400 MHz at 30°C. 25 mg of the samples was either solubilized or swollen in 1 ml of toluene-d8, and TMS was used as a reference.

- ***Rheological measurements***

Low-deformation rheological analyses were performed on an ARES 4800 with parallel plate geometry (diameter 25 mm). Discs were cut into sample plates obtained after molding at 160°C.

Firstly, samples were submitted to a strain sweep test at 160°C, at a frequency of 10 $rad \cdot s^{-1}$, from 0.01% to 30% of strain, in order to determine the linear domain of strain. Secondly, a time sweep test was carried out at 160°C, at a frequency of 10 $rad \cdot s^{-1}$, at a strain corresponding to the linear domain in order to check that the sample rheology did not change during the time of the analysis. Finally, dynamic frequency sweep tests were performed at 160°C, at a strain of 1% corresponding to the linear domain, from 100 to 0.01 $rad \cdot s^{-1}$.

- ***Swelling test***

Swelling experiments were carried out by immerging the EPDM-based samples in toluene. The system was allowed to reach equilibrium, and the amount of solvent absorbed by the sample was measured using gravimetric or volumetric methods. The sample was then rinsed and dried. The non-crosslinked polymer chains were extracted and the sample weight was measured [53-55]. The insoluble fraction and amount of swelling are defined to determine the crosslinking density by the equation:

$$Q = \frac{V_s}{V_i} \quad (1)$$

where Q is the coefficient of swelling, V_s is the swelling volume and V_i is the initial volume before the swelling experiment. This equation can be rewritten as:

$$Q = \frac{\frac{m_s}{\rho_s} + \frac{m_p}{\rho_p}}{\frac{m_p}{\rho_p}} \quad (2)$$

where m_s is the mass of toluene absorbed by the EPDM and $\rho_s = 867\ \text{kg.m}^{-3}$ is the density of toluene, m_p the mass of the EPDM sample and $\rho_p = 860\ \text{kg.m}^{-3}$ its density.

From the equilibrium swelling theory of Flory and Rehner [56], the crosslinking density υ can be calculated and expressed in mol·m^{-3} [57]:

$$\upsilon = -\frac{ln(1-\upsilon_p)+\upsilon_p+\chi\upsilon_p^2}{V_{ms}\left(\upsilon_p^{1/3}-\frac{\upsilon_p}{2}\right)} \quad (3)$$

where $V_{ms} = 106.26\ \text{ml} \cdot \text{mol}^{-1}$ is the molar volume of solvent, υ_p is the volume fraction of EPDM in the swollen mass (i.e., the inverse of the swelling rate, $1/Q$), and χ is the interaction parameter between the polymer and solvent, sometimes referred to as the Flory–Huggins interaction parameter. In the present work we used $\chi = 0.49$, as generally assumed in the literature [58-62]. For the calculation of the insoluble fraction, the EPDM, the reagent and the vegetable oil will all be accounted for, because all these compounds are able to react during the heat treatment.

- ***Exudation test***

To measure the extent of exudation, a sample of EPDM was mixed until full incorporation with 30 wt% of oil. The sample mass was measured, and it was then placed in an oven at 80°C for 7 days. The sample was then wiped with absorbent paper to remove excess oil from the surface, and the sample mass was measured again. The mass difference allowed us to define the oil loss by exudation [63, 64].

- ***Compression set measurements***

Compression set testing [65] is used to determine the ability of elastomeric materials to maintain elastic properties after prolonged compressive stress. The test measures the permanent deformation of the specimen after it has been exposed to compressive stress for a set time period. A small cylinder of crosslinked EPDM sample was placed between the

parallel plates of the DMA (DMA Q800, TA Instruments, with compression modulus) and reheated to a temperature of 100°C. The shape of the cylinder (radius R = 5 mm and thickness e = 2 mm (I_0)) was rigorously elaborated and size-controlled. The software was programmed to impose a nominal deformation of $\varepsilon_{0,n} = 0.25$ (I_1) for 24 h at 100°C.

After this loading time, the sample was removed from the plates and cooled down to room temperature by placing it on a surface with poor thermal conduction properties for 30 min before measuring the final thickness (I_2). The compression set is expressed as a percentage of the original deflection, DRC [66]:

$$DRC = \frac{I_0 - I_1}{I_0 - I_2} * 100 \text{ with } \varepsilon_{0,n} = \frac{I_0 - I_2}{I_0} \quad (4)$$

- ***Tensile test***

Tensile tests were carried out using normalized dumb-bell-shaped samples of type H2. The tests were performed using an MTS Criterion model 43 tensile-testing machine, at a crosshead speed of 500 mm/min^{-1}, at 20°C and 50% relative humidity. At least five specimens were tested for each EPDM formulation.

III- Results and discussion

The thiol–ene reaction is a well-known reaction. The addition of a thiol to an unsaturated olefin was shown by Posner in 1905 [67]. Thiol–ene reactions involve the addition of a S-H bond to a double or triple bond (Fig. 5) by either a metal-catalyzed complexation [68] or free radical mechanism [19, 69, 70]. Thiol–ene reactions are essentially the sulfur version of the hydrosilylation reaction. Because the reactions are efficient, high-yielding, and tolerant to various solvents and functional groups, many researchers now consider the thiol–ene reaction to be a "click" reaction.

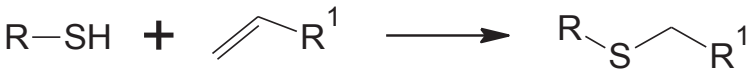


Fig. 5. Scheme of a thiol-ene reaction

This reaction is expected to occur between the unsaturated groups of the norbornene moiety from the EPDM polymer matrix and the FFM (Fig. 6). This experiment was carried out at 160°C in the internal mixer. Note that at high temperatures (> 120°C), as demonstrated by Shostakovsky et al. [71], this reaction is poorly selective [72]. However, this reaction remains interesting for the grafting of FFM onto the EPDM matrix. Moreover, in the work of

Hoyle et al. [73], it has been noted that the norbornene function is one of the more reactive in the thiol–ene reaction.

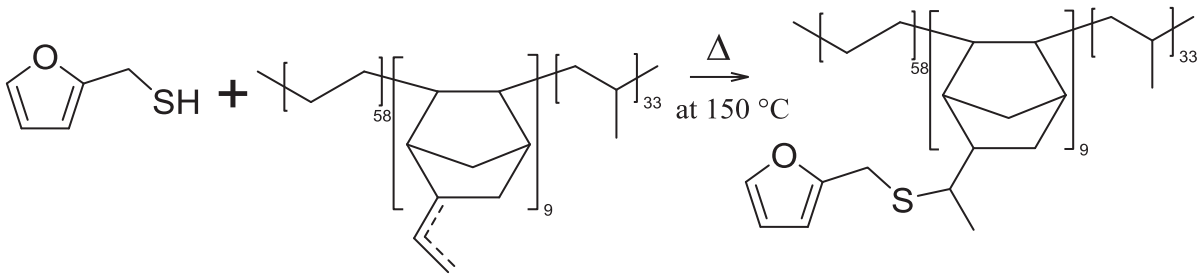


Fig. 6. Expected thiol-ene reaction between the FFM and EPDM

In the second step, 30 wt% of tung oil is introduced into the internal mixer at the same temperature. The mixture is stirred for a few minutes until complete incorporation of the vegetable oil. During this step, the residual FFM is able to react with the tung oil double bonds. The increase of the temperature up to 250–260°C aims to initiate the Diels–Alder reaction between the furfuryl group from the previously grafted species and the tung oil double bonds (Fig. 7). Based on previous work [52], a standoil reaction of the tung oil might also be observed under these processing conditions, as will be discussed later in this study.

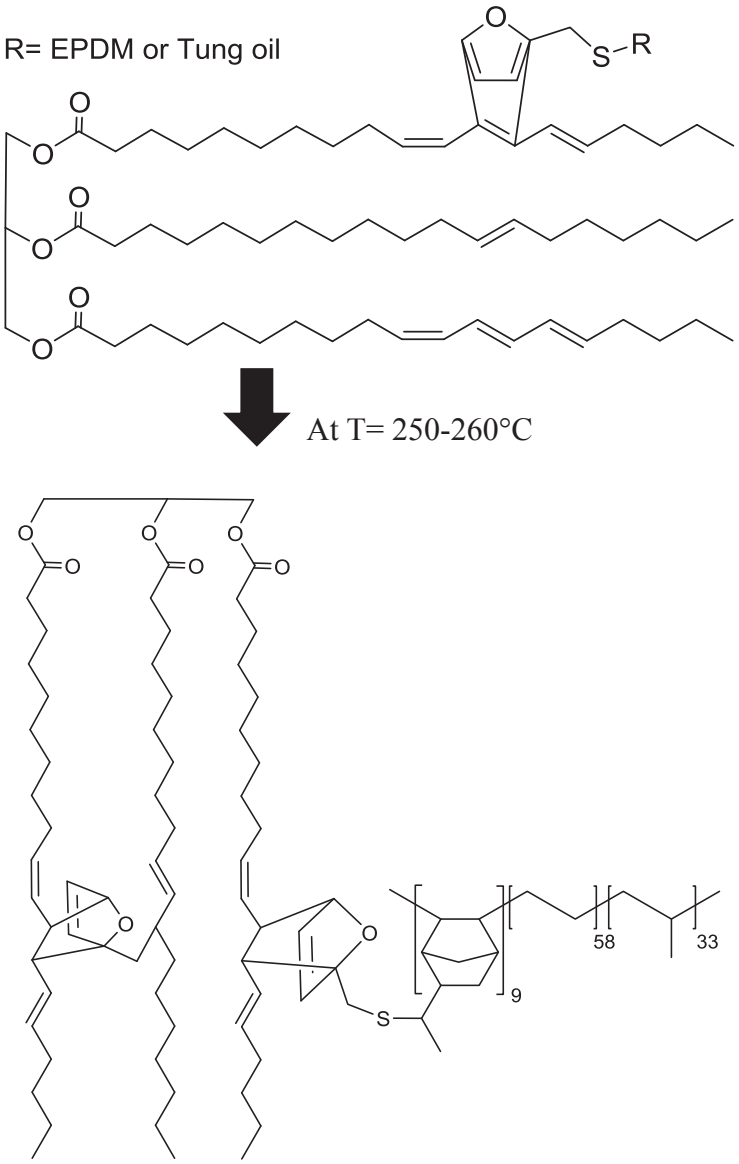


Fig. 7. Diels-Alder reaction between the Tung oil fatty acid and the EPDM grafed FFM

III-1) EPDM crosslinking with the FFM under dynamic conditions

The efficiency of these chemical reactions can be deduced from the variation of the torque versus time observed during the experiment carried out in the internal mixer (Fig. 8).

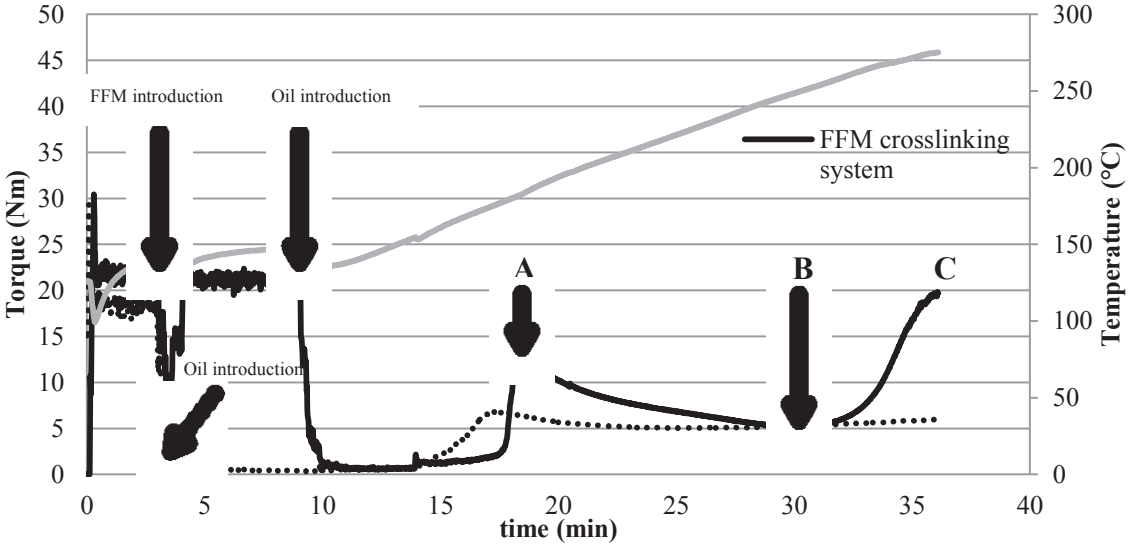


Fig. 8. Torque and temperature evolutions versus time (min) during EPDM crosslinking reaction in a internal mixer with the FFM (solid line) and without the FFM (dotted line).

Different observations from these curves can be made. At t = 0 min the EPDM matrix is introduced into the internal mixer at 140°C and stirred for 3 min. At t = 3 min, 6 wt% of FFM is added to initiate the crosslinking system (solid line), which corresponds to a molar ratio of 1.3/1 of -SH/norbornene. For the crosslinking system, the formulation is stirred additionally for 5 min at 140°C to enhance the grafting reaction of the FFM onto the EPDM matrix. The torque remains constant at around 21 N·m. At t = 10 min, 30 wt% of tung oil is injected and the temperature is increased to 250°C. During this phase the phenomenon of lubrication leads to a decrease of the torque down to 0 N·m until the oil has penetrated the EPDM matrix. The significant increase of the torque to 12.5 N·m, observed at 18 min (point A on the curve), corresponds to the disappearance of the lubrication effect. The decrease of the torque between t = 18 min and t = 30 min (between points A and B) is the result of the homogenization effect of the plasticizer, and of the increase of temperature. At t = 30 min (point B), the critical temperature of 250°C is reached and the crosslinking reaction (according to Fig. 8) occurs, leading to a sharp increase of the torque. Specifically, the torque increases from 5 N·m (point B) to 20 N·m (point C) within 5 minutes. For the system without FFM (dotted line), at t = 3 min, 30 wt% tung oil is added, leading to the same phenomenon as observed previously. The time of diffusion of tung oil into the EPDM matrix is 15 min, whereas it was around 8 min in the previous case. Thus the time of diffusion is considerably reduced by the presence of the FFM, which may be due to furfuryl functions acting as a compatibilizing agent. At t = 30 min and T = 250°C, no significant increase of the torque is

observed, contrary to the system with FFM. This result seems to confirm that the crosslinking reaction is effective, due to the Diels–Alder reaction. Based on our previous work, two other reactions may also contribute to the densification of the network crosslinking. In this range of temperature, the standoil reaction of the tung oil [52] can take place. This intra-molecular homopolymerization of tung oil is used to create covalent bonds within the vegetable oil, as shown in Fig. 9.

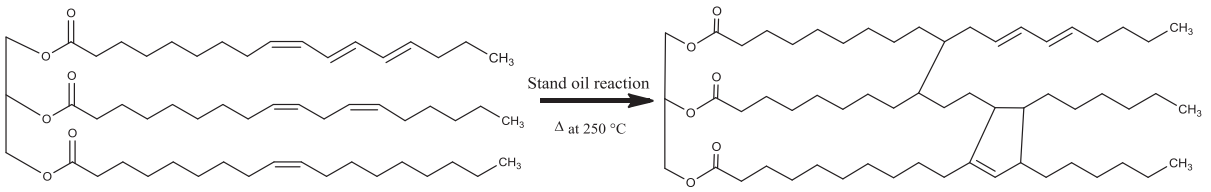


Fig. 9. Stand oil reaction on Tung oil

Furthermore, at 250°C we can consider that all these reactions may occur: the FFM can react with the EPDM double bonds but also with the vegetable oil double bonds. The Diels–Alder reaction is possible between the FFM and the tung oil. Finally, inside the tung oil the fatty acid can react by the standoil reaction. If we take into account all these reactions, we can consider that the final structure of the crosslinked system after thermal curing at 250°C can be represented as in Fig. 10.

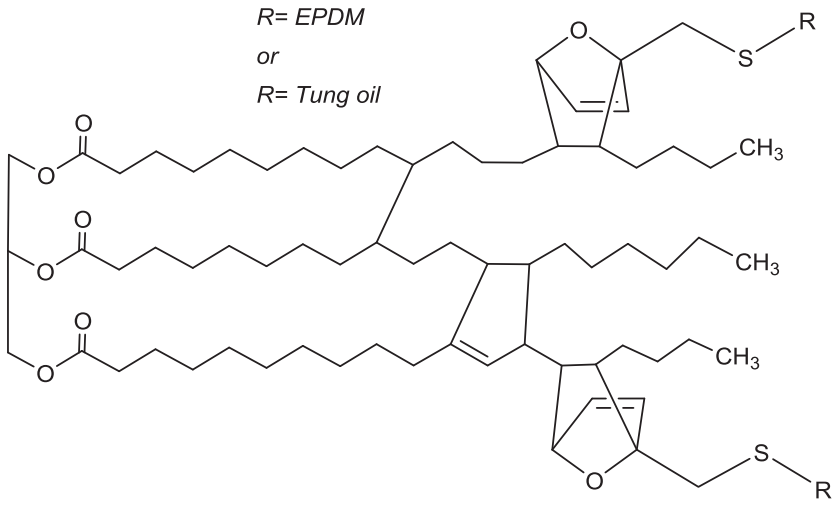


Fig. 10. Theoretical structure after thermal curing at 250°C of the system EPDM/FFM and Tung oil

This sample based on the EPDM/FFM/tung oil system was analyzed by the swelling test before (point A on Fig. 8) and after heat treatment (point C on Fig. 8). Before heat treatment, no insoluble fraction was detected. In contrast, after heat treatment, an insoluble fraction of 72 ± 2 wt% was measured (this insoluble fraction must be balanced by the tung

oil, as it is able to react), for a swelling ratio of 9.4 and a density of crosslinking of 12.7 ± 0.2 $mol \cdot m^{-3}$. This high crosslinking density is evidence of the good reactivity of this system. For the sample without FFM after heat treatment (point C on the curve), no insoluble fraction was detected.

The chemical structure of the EPDM/FFM/tung oil system before (Fig. 11, corresponding to point A on Fig. 8) and after heat treatment at 250°C for 5 min (Fig. 12, corresponding to point C on Fig. 8) was determined by liquid ^{1}H NMR spectroscopy. We focused especially on four spectral zones:

- Around 3.22 ppm, corresponding to the proton resonance from the C**H**$_2$-SH group in the α-position of the –SH.
- Around 3.37 ppm, corresponding to the proton resonance from the –S-C**H** group in the α-position of the –S for the thiol–ene reaction.
- 5.00–5.50 ppm, corresponding to proton resonance from the norbornene double bond group for the thiol–ene reaction and mono-unsaturated groups from the fatty acid.
- 5.50–6.25 ppm, corresponding to the proton resonance from the conjugated double bonds from the tung oil and from the furfuryl group for the Diels–Alder reaction and other contributing radical reactions.

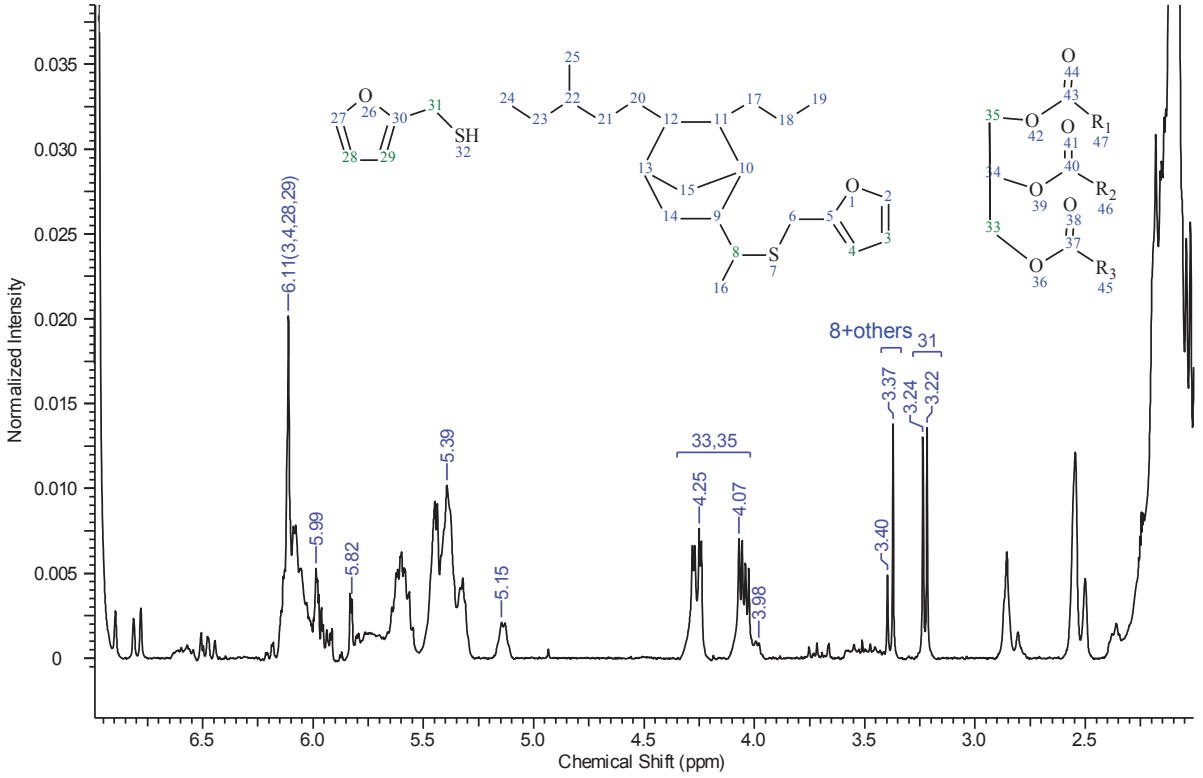


Fig. 11. Liquid ^{1}H NMR spectrum of Tung oil, FFM and EPDM formulation no curing, center between 2.0 and 7.0 ppm (toluene d-8 at 30°C). Sample was taken at t= 17 min (point A on the Fig. 8)

The signal at around 3.37 ppm confirms the grafting of the thiol function onto the double bond. The high intensity of the signal at 6.11 ppm, corresponding mainly to the unsaturated proton resonance from tung oil and from the furfuryl group, seems to show that the Diels–Alder reaction has not occurred.

The spectrum (Fig. 12) of the EPDM/FFM/tung oil system (of which the soluble part is 30 wt%) cured at 250°C for 5 min and then swollen in deuterated toluene is compared with the previous one (Fig. 11) to determine the rate of reaction that occurred during the heat treatment. The following assessments can be made:

- In the range 3.0–3.5ppm, we observe a complete absence of the signals corresponding to the proton resonance from the CH_2 group in the α-position of the –SH or S-R bonds, which indicates that only the thiol derivative contributes to the insoluble fraction.
- In the range 4.05–4.25 ppm, the signals corresponding to the proton resonance of the tri-ester functions from the tung oil are still detectable.
- In the range 5.50–6.25 ppm, the signals corresponding to the proton resonance of tri- and di-conjugated double bonds from the tung oil have disappeared. This

absence from the soluble fraction is also in agreement with the expected reactions. We also do not observe the signal attributed to the furfuryl function.

- In the range 5.00–5.50ppm, the signals corresponding to the proton resonance of the fatty acid mono-unsaturated groups and of the residual double bonds from the norbornene moiety are still in the soluble part.

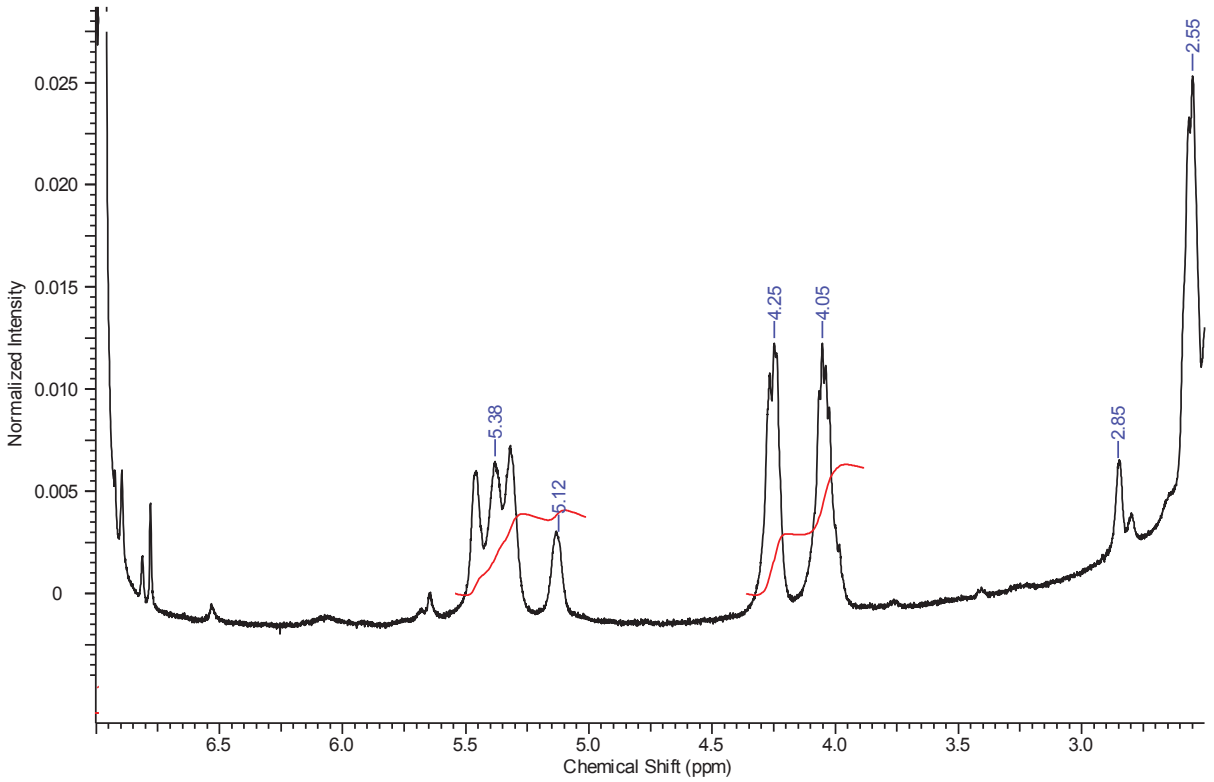


Fig. 12. Liquid ^{1}H NMR spectrum of the system EPDM/FFM and Tung oil curing at 250°C during 5min, center between 2.5 and 7.0 ppm (toluene d-8 at 30°C). Sample was taken at t= 35 min (point C on the Fig. 8)

In conclusion, the absence of signals corresponding to the proton resonance of groups in the α-position of the sulfur atom in the soluble part may confirm the efficiency of the expected thiol-based reactions. The Diels–Alder reaction between the tung oil and the FFM and the standoil reactions are also confirmed by the absence of proton resonance signals corresponding to furfuryl functions and conjugated di- and tri-unsaturated groups in the fatty acid between 5.5 and 6.25 ppm. All these observation are in agreement with the expected reactions.

These results allowed us to determine the relative composition of this soluble fraction. From the peak intensity, the results showed a relative composition of 20 and 80 wt% of EPDM and vegetable oil, respectively. The oil fraction was in the majority composed of residual saturated and mono-unsaturated fatty acids.

III-2) FFM versus classical peroxide crosslinking

In the previous part, we have considered a crosslinking reaction carried out under shearing (i.e., under dynamic conditions) in an internal batch mixer. However, to obtain homogeneous samples, in particular to characterize the mechanical properties, the materials are compression-molded and crosslinked under a heated press (i.e., under static conditions). For that process, we first have to optimize the curing time to reach the highest rate of crosslinking. Thus, the EPDM was formulated with 30 wt% of tung oil and 6 wt% of FFM and molded at T = 140°C. These samples were then cured at 250°C for different lengths of time and analyzed by rheology (Fig. 13).

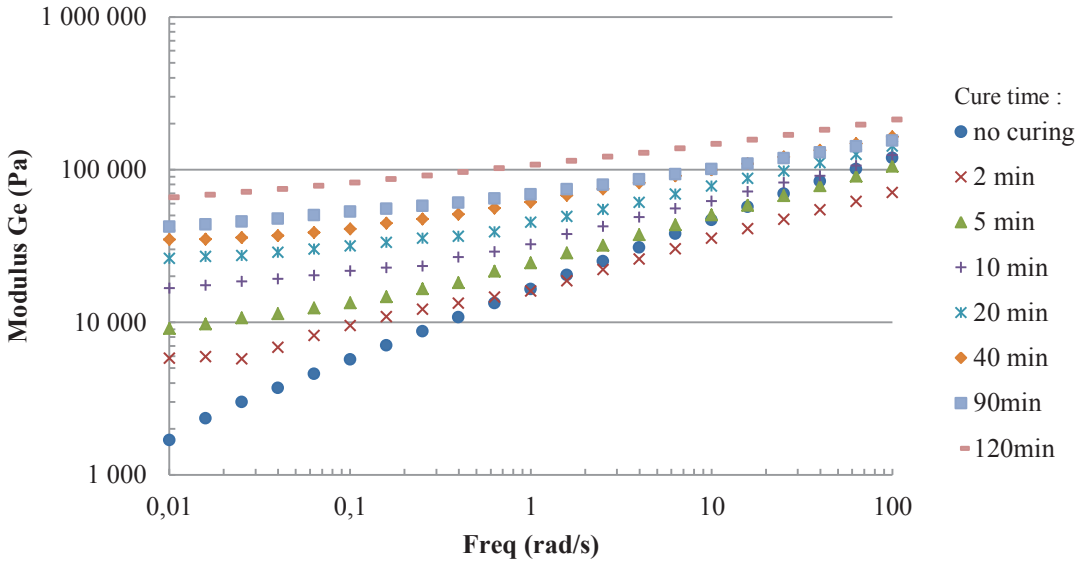


Fig. 13. Variation of the elastic modulus G_e versus freq (rad/s) at 160°C for a EPDM formulated with 30%wt of Tung oil and 6%wt of FFM and cured at 250°C during different time

The analysis of these curves revealed a storage modulus that increased with the curing time. The highest value ($G_e = 6.6 \times 10^4$ Pa at 0.01 rad·s^{-1}) was obtained for 120 min of curing at 250°C, which corresponds to the modulus reached within a few minutes under dynamic conditions ($G_e = 4.0 \times 10^4$ Pa at 0.01 rad·s^{-1}). This curing time was chosen to compare the FFM-based system with the DCP- (0.5 or 1 wt%) based references cured classically at 180°C for 10 min.

a) Determination of the crosslinking density and viscoelastic behavior

From the swelling experiments, the insoluble fraction and the crosslinking densities were determined and compared (Table 1).

Table 1. Swelling results for different EPDM based systems (FFM/Tung oil and peroxide)

Sample	Insoluble (%)	υ_p	υ mol/m^3	Ge (Pa) at 0.01 rad/s
6% FFM/ 30% Tung/250°C/120min	79±2	0.05	1.7±0.1	4x10^4
0.5% DCP/30% Torilis®/180°C/10min	50±2	0.02	0.3±0.1	1x10^4
1.0% DCP/30% Torilis®/180°C/10min	64±2	0.05	1.3±0.1	6x10^4

Compared with the FFM-based systems, the EPDM samples crosslinked with DCP had lower insoluble fractions, with 50.0% for 0.5 wt% of DCP and 64% for 1.0 wt% of DCP. Similarly, the swelling ratios were higher, with 45.8 for 0.5 wt% of DCP and 22.1 for 1.0 wt% of DCP. The υ values were also markedly different, with a low crosslinking density of around 0.3 mol/m^3 for 0.5 wt% of DCP. In contrast, the υ value for 1.0 wt% of DCP was closer to the one obtained with the FFM: 1.3 and 1.7 mol/m^3 respectively. These results are consistent with the values obtained for sulfur crosslinking-based systems consisting of sulfur-accelerators (2-mercaptobenzothiazole, tetramethylthiuram disulfide, *N*-cyclohexyl-2-benzothiazole sulfonamide, dipentamethylene thiuramtetrasulfide, zinc dimethyldithiocarbamate...) and sulfur with different accelerator/sulfur ratios and vulcanization times, which had insoluble fractions around 75% [74]. These results highlight the efficient crosslinking of the EPDM matrix with thiol derivatives and vegetable oil. The results also confirm that the thiol system is relatively similar to the EPDM-crosslinked reaction with 1.0 wt% of DCP.

To check the efficiency of our crosslinking system, the samples prepared previously were analyzed by rheology in terms of the variation of elastic modulus versus frequency at 160°C (Fig. 14).

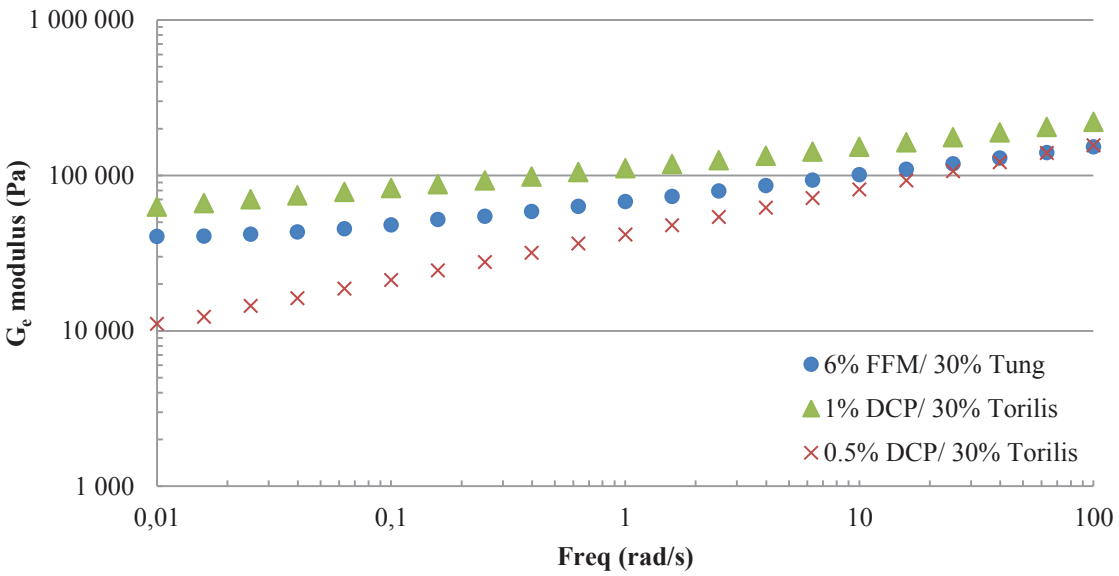


Fig. 14. Variation of the elastic modulus G_e versus freq (rad/s) at 160°C for EPDM samples formulated with 6%wt of FFM, 1.0%wt of DCP and 0.5%wt of DCP by static crosslinking.

First, the curves show, as expected, a difference of rheological behavior depending on the two concentrations of DCP used. At 0.01 rad·s^{-1} the difference between the equilibrium shear moduli is pronounced: the G_e is 1×10^4 Pa for 0.5 wt% of DCP and 6×10^4 Pa for 1.0 wt% of DCP. Moreover, when comparing the DCP- and FFM-based systems, we notice that the modulus value of the FFM-based system at 0.01 rad·s^{-1} is close to the one obtained with 1.0 wt% of DCP, with a value of 4×10^4 Pa. These rheology analyses confirm that the thiol-based systems have a crosslinking efficiency that is close to the 1.0 wt% DCP-based system.

Lastly, a common problem observed when introducing vegetable oil into an EPDM matrix is the exudation of the final product. When submitting our samples to the exudation test described previously, carried out at 80°C, almost no mass loss was observed, with around 0.8% and 1.0% respectively for the DCP and FFM crosslinking-based systems, which can be considered negligible.

b) Mechanical properties

Table 2 shows the results of the compression set obtained with the same samples compressed by 25% at 100°C for 24 h.

It can be observed that the thiol-based system has a shape recovery after 30 min of 58%, close to the value obtained with 1.0 wt% of DCP (61%). For the formulation with 0.5 wt% of DCP, the value is higher, at 72%. These results correspond to a formulation composed

with a range between 10 and 30 phr of resol [75] and confirm again the similar behavior between the FFM- and 1 wt% of DCP-based systems.

Table 2: Compression set and tensile test results for different EPDM formulation with Thiol and DCP based systems

	0.5% DCP/30% Torilis®/180°C/10 min	***1.0% DCP/30% Torilis®/180°C/10 min***	***6% FFM/ 30% Tung /250°C/120min***
DRC (%)	72±2	61±2	58±2
Max Stress (MPa)	0.7 ± 0.1	2.6±0.3	1.0±0.1
Breaking strain (%)	****	2500±90	650±100
Modulus of Elasticity (MPa)	0.4±0.1	0.4±0.1	0.7±0.1

The final mechanical analysis performed on the crosslinked samples was the tensile test. Results and curves are depicted in Table 2 and Fig. 15 respectively.

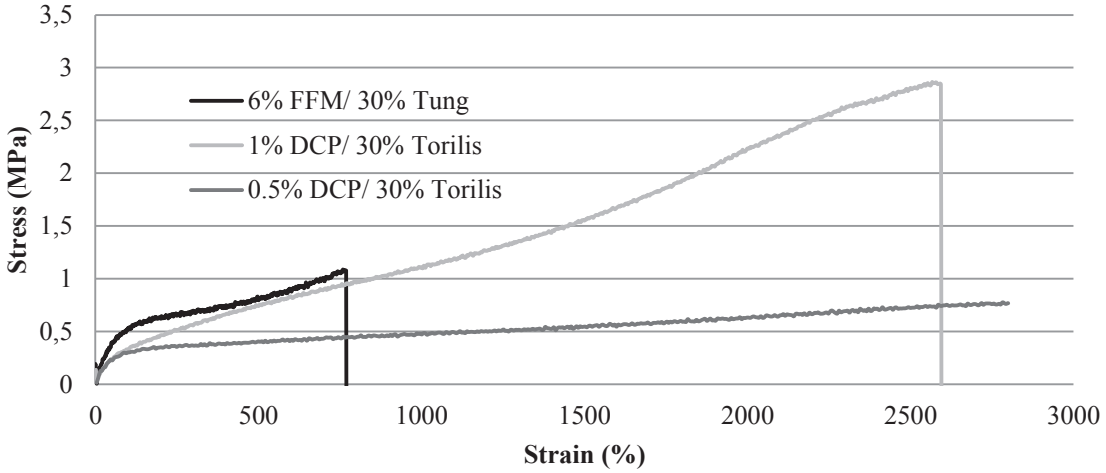


Fig. 15. Tensile curve stress versus strain at room temperature for a elongation speed of 500mm/min

The analysis of these results reveals different mechanical behaviors between the thiol- and DCP-based systems. With the thiol system, the modulus of elasticity is slightly increased, with a value of 0.72 MPa versus 0.40 MPa for the DCP-based formulation. The maximum stress and the breaking strain are relatively weak compared with the DCP, with a value of 1.0 MPa of maximum stress for the FFM and 2.6 MPa for 1.0 wt% of DCP. Concerning the strain at break, the values are over 2,700% for 0.5 wt% of DCP and around 2,500% for 1.0 wt% of DCP, compared with the value of around 630% obtained with the FFM. These low values may be explained in part by the nature of the connections generated by the thiol–ene and vegetable oil crosslinking reactions.

III-3) Alternative thiol-based system

In this part, we used the same approach as previously, but substituted the FFM with DiFFM. DiFFM has a disulfide function, with a dissociation energy of the disulfide bonds of 51.2 ± 3 Kcal·mol^{-1} (for comparison, the dissociation energy of the C-C bonds is 86.9 ± 1.3 Kcal·mol^{-1} [76-78]). At high temperature the weak covalent bonds dissociate to create two radicals, –S•, which can react on EPDM or tung oil double bonds as represented in Fig. 16. Furthermore, the higher boiling point of this reagent makes it more suitable for use at high temperature.

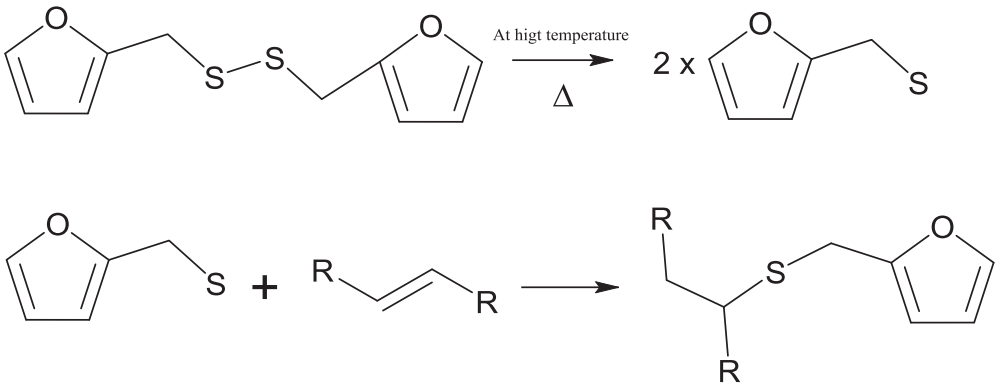


Fig. 16. Reactivity of the DiFFM at high temperature on double bonds

a) Comparison between FFM and DiFFM

The variation in torque was measured and compared with the previous system as shown in Fig. 17.

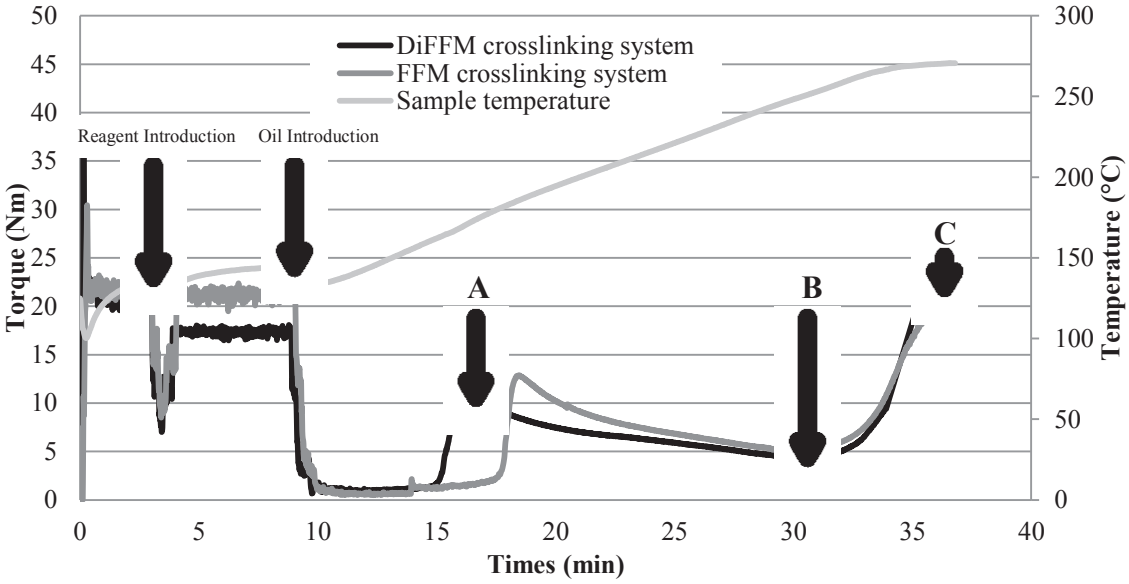


Fig. 17. Torque (Nm) and temperature (°C) evolutions versus time (min) during crosslinking process with the DiFFM comparing with the FFM based system.

Compared with the behavior of the FFM-based system (Fig. 8), we can notice several differences. At t = 10 min the same quantity of tung oil is incorporated. However, the time taken to reach a complete and homogeneous incorporation is slightly shortened with DiFFM compared with FFM (point A on the curve, Fig. 17). During the curing up to 250°C, the torque increases in the same way, from 4.40 N·m to 21.5 N·m in 5 minutes (between points B and C on the curve). Furthermore, when comparing the DiFFM- with the FFM-based systems, the results highlight the better reactivity of the DiFFM, with a 93 $\pm$ 1 % insoluble fraction and a swelling of 8.5 $\pm$ 0.3 ($\upsilon = 16.0 \pm 0.2$ mol·m^{-3}), versus 72 $\pm$ 2 % insoluble fraction for FFM and a swelling of 9.4 $\pm$ 0.2 ($\upsilon = 12.7 \pm 0.2$ mol·m^{-3}). These results confirm the previous observations and the higher reactivity of the DiFFM.

The chemical structure of the 7 wt% soluble part of the EPDM/tung oil/DiFFM sample after heat treatment at 250°C for 5 min (point C, Fig. 17) was determined by liquid ^{1}H NMR spectroscopy (Fig. 18).

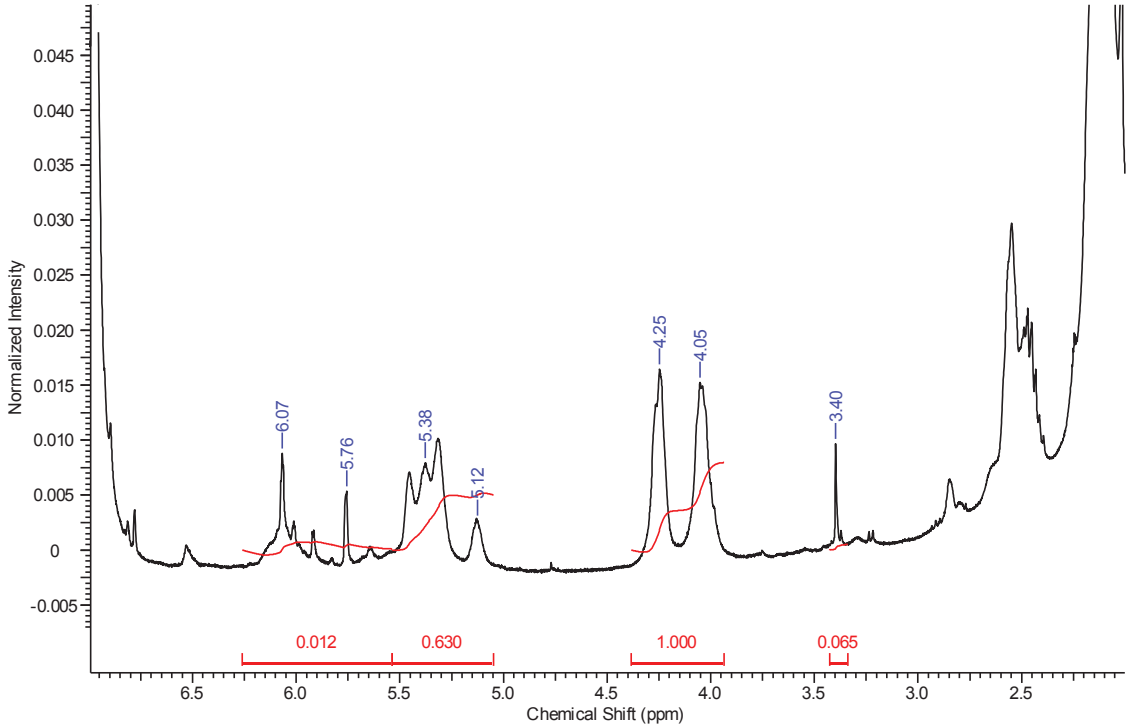


Fig. 18. Liquid ^{1}H NMR spectrum of the system Tung oil, DiFFM and EPDM formulation curing at 250°C during 5min, center between 2.0 and 7.0 ppm (point C Fig. 17)

The spectrum of the system (of which the soluble part is 7 wt%) swollen in deuterated toluene allows the following observations:

- At 3.40 ppm, the proton resonance signal from CH_2 at the α-position of the sulfur atom indicates the presence of grafted thiol functions in the soluble part.
- At 4.05 and 4.25 ppm, the proton resonances of the tri-ester functions from the tung oil are still detectable.
- In the range 5.0–6.0 ppm, we still observe proton resonance from the tung oil unsaturated groups, residual double bonds of norbornene, and residual furfuryl functions.

The signals corresponding to proton resonance from CH_2 at the α-position of the sulfur atom in the soluble part show that the reaction is not complete, which is also confirmed by the furfuryl proton resonance at 6.07 ppm. The Diels–Alder reaction between the tung oil and the DiFFM and the standoil reaction are, however, confirmed by the low intensity of the proton signals corresponding to di- and tri-unsaturated fatty acid groups between 5.50 and 6.25 ppm in comparison with the intensity of the tri-ester proton signals at 4.05 and 4.25 ppm.

The results show a relative composition of 10 and 90 wt% of EPDM and vegetable oil respectively, which is similar to the FFM system. The oil fraction in the soluble part was in

the majority composed of saturated and poly-unsaturated fatty acids, contrary to the FFM system composed only of saturated and mono-unsaturated fatty acids.

To test the mechanical properties of the DiFFM system, the sample was analyzed by rheology in terms of the variation of elastic modulus versus frequency at 160°C, and compared with the characteristics of the FFM-based system (Fig. 19).

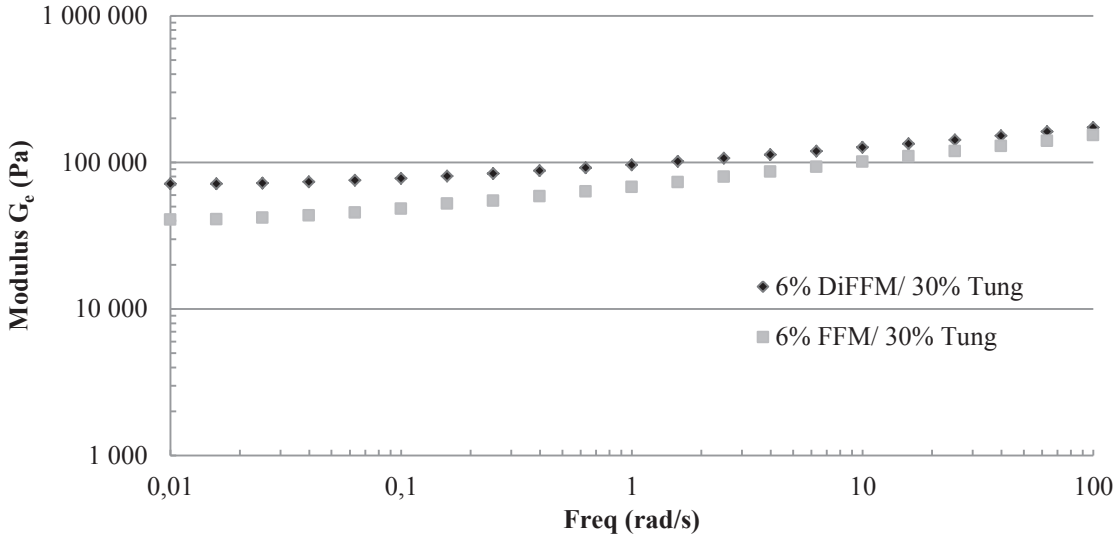


Fig. 19. Variation of the elastic modulus G_e versus freq (rad/s) at 160°C for an EPDM samples formulated with 30%wt of Tung oil and 6%wt of DiFFM and curing at 250°C in internal mixer. Comparison with the FFM system

Focusing on these curves, we can notice that the rheological behaviors are similar, with a slightly higher modulus for the DiFFM system. We observe an equilibrium shear modulus G_e between 4×10^4 and 10^5 Pa, which is consistent with a crosslinked system.

Concerning the compression set, similar recoveries after 30 min are observed for FFM and DiFFM, with respectively 58% and 57%. In conclusion, the DiFFM system presents behavior similar to the FFM one for linear elasticity and recovery properties. Moreover, we can observe a better density of the crosslinking network for the DiFFM system, and its soluble part has a slightly different composition. Hence the NMR analysis shows a residual DiFFM contribution in the soluble part, contrary to the FFM, which may indicate a poorer control of the reactivity of DiFFM.

IV- Conclusion

In this study, we have developed an alternative method to crosslink the EPDM matrix with a reactive vegetable oil, tung oil, and a reactive agent, 2-furanmethanethiol (FFM),

obtained from agribusiness. We principally used a combination of the thiol–ene and Diels–Alder reactions to graft the FFM onto the EPDM and react on the tung oil double bonds. We compared these crosslinking systems to references with 0.5 or 1.0 wt% of DCP and 30 wt% of mineral plasticizer. The thiol system was processed in an internal mixer in three successive steps and thermally controlled to activate the thiol–ene reaction and the standoil reaction on the tung oil. To increase the reactivity of the reactive agent, we also used DiFFM, which at high temperature can dissociate into two radicals, –S•, and react quickly with the double bond. These reactions were confirmed by liquid ^{1}H NMR analysis. Thereafter the samples were analyzed using different mechanical and chemical tests. In all cases, we observed a higher crosslinking density compared with the 0.5 and 1.0 wt% DCP formulations. The compression set and rheology analysis showed similar or superior results to those obtained with 1.0 wt% of DCP. These results are encouraging and demonstrate that a green crosslinking, based on a reactive vegetable oil and a reactive agent used in food processing, can create a dense crosslinking network, having good mechanical and chemical properties.

Acknowledgments: We thank Novance and Activation for providing the neat and the modified oils, and Hutchinson companies for their work on EPDM polymers. We also thank Evea for life cycle analysis of different oils, the poles of competitiveness Techtera, Elastopole and IAR for their support and finally the Humevere project.

V- References

1. Choi, S.-S. and J.-E. Ko, *Influence of thermal aging on pyrolysis pattern of carbon black-filled NR composite.* Macromolecular Research, 2007. **15**(5): p. 482-485.
2. Kim, M., et al., *Life time prediction of rubber gasket for fuel cell through its acid-aging characteristics.* Macromolecular Research, 2007. **15**(4): p. 315-323.
3. Krejsa, M.R. and J.L. Koenig, *A Review of Sulfur Crosslinking Fundamentals for Accelerated and Unaccelerated Vulcanization.* Rubber Chemistry and Technology, 1993. **66**(3): p. 376-410.
4. Chakraborty, S.K., A.K. Bhowmick, and S.K. De, *Mixed Cross-Link Systems in Elastomers.* Journal of Macromolecular Science, Part C, 1981. **21**(2): p. 313-332.
5. Van Duin, M. and A. Souphanthong, *The chemistry of phenol-formaldehyde resin vulcanization of EPDM: part I. Evidence for methylene crosslinks.* Rubber Chemistry and Technology, 1995. **68**(5): p. 717-727.
6. Layer, R.W., *A Postcrosslinking Accelerator System for Natural Rubber Based on Thiocarbamyl Sulfenamides.* Rubber Chemistry and Technology, 1987. **60**(1): p. 89-101.
7. Zaper, A.M. and J.L. Koenig, *Solid State Carbon-13 NMR Studies of Vulcanized Elastomers. II, Sulfur Vulcanization of Natural Rubber.* Rubber Chemistry and Technology, 1987. **60**(2): p. 252-277.
8. Salgueiro, W., et al., *Dependence of the network structure of cured styrene butadiene rubber on the sulphur content.* Polymer, 2004. **45**(17): p. 6037-6044.
9. Choi, S.-S., I.-S. Kim, and C.-S. Woo, *Influence of TESPT content on crosslink types and rheological behaviors of natural rubber compounds reinforced with silica.* Journal of Applied Polymer Science, 2007. **106**(4): p. 2753-2758.
10. Manik, S.P. and S. Banerjee, *Effect of Sulfur and Dicumyl Peroxide on Vulcanization of Natural Rubber with Tetramethylthiuram Disulfide and Zinc Oxide.* Rubber Chemistry and Technology, 1970. **43**(6): p. 1294-1310.
11. González, L., et al., *Crosslink Reaction Mechanisms of Diene Rubber with Dicumyl Peroxide.* Rubber Chemistry and Technology, 1996. **69**(2): p. 203-214.
12. Morrison, N.J. and M. Porter, *Temperature Effects on the Stability of Intermediates and Crosslinks in Sulfur Vulcanization.* Rubber Chemistry and Technology, 1984. **57**(1): p. 63-85.
13. Mousa, A. and J. Karger-Kocsis, *Rheological and Thermodynamical Behavior of Styrene/Butadiene Rubber-Organoclay Nanocomposites.* Macromolecular Materials and Engineering, 2001. **286**(4): p. 260-266.
14. Coran, A.Y., *Vulcanization: conventional and dynamic.* Rubber Chemistry and Technology, 1995. **68**(3): p. 351-375.
15. Jacob, M., S. Thomas, and K.T. Varughese, *Mechanical properties of sisal/oil palm hybrid fiber reinforced natural rubber composites.* Composites Science and Technology, 2004. **64**(7): p. 955-965.
16. Katzanevas, F., *La vulcanisation.* IFOCA, 1994: p. 33.
17. Lowe, A.B., *Thiol-ene "click" reactions and recent applications in polymer and materials synthesis.* Polymer Chemistry, 2010. **1**(1): p. 17-36.
18. Lowe, A.B., *Thiol-ene "click" reactions and recent applications in polymer and materials synthesis: a first update.* Polymer Chemistry, 2014. **5**(17): p. 4820-4870.
19. Hoyle, C.E. and C.N. Bowman, *Thiol-Ene Click Chemistry.* Angewandte Chemie-International Edition, 2010. **49**(9): p. 1540-1573.
20. Huang, J.-L., C.-J. Li, and D.G. Gray, *Functionalization of cellulose nanocrystal films via "thiol-ene" click reaction.* RSC Advances, 2014. **4**(14): p. 6965-6969.

21. Tingaut, P., R. Hauert, and T. Zimmermann, *Highly efficient and straightforward functionalization of cellulose films with thiol-ene click chemistry.* Journal of Materials Chemistry, 2011. **21**(40): p. 16066-16076.
22. Nielsen, L.J., et al., *Dual fluorescent labelling of cellulose nanocrystals for pH sensing.* Chemical Communications, 2010. **46**(47): p. 8929-8931.
23. Zhao, G.-L., et al., *Heterogeneous "Organoclick" Derivatization of Polysaccharides: Photochemical Thiol-ene Click Modification of Solid Cellulose.* Macromolecular Rapid Communications, 2010. **31**(8): p. 740-744.
24. Pojman, J.A., et al., *Frontal polymerization with thiol-ene systems.* Macromolecules, 2004. **37**(3): p. 691-693.
25. Roper, T.M., et al., *Influence of the alkene structure on the mechanism and kinetics of thiol-alkene photopolymerizations with real-time infrared spectroscopy.* J. Polym. Sci. Part A: Polym. Chem, 2004. **42**(24): p. 6283-6298.
26. Hoyle, C.E., R.D. Hensel, and M.B. Grubb, *Laser-initiated polymerization of a thiol-ene system.* Polymer Photochemistry, 1984. **4**(1): p. 69-80.
27. Hoyle, C.E., R.D. Hensel, and M.B. Grubb, *Temperature-dependence of the laser-initiated polymerization of a thiol-ene system.* J. Polym. Sci. Part A: Polym. Chem, 1984. **22**(8): p. 1865-1873.
28. Lee, T.Y., et al., *Thiol-ene photopolymerization kinetics of vinyl acrylate/multifunctional thiol mixtures.* Macromolecules, 2004. **37**(10): p. 3606-3613.
29. Hoyle, C.E., T.Y. Lee, and T. Roper, *Thiol-enes: Chemistry of the past with promise for the future.* J. Polym. Sci. Part A: Polym. Chem, 2004. **42**(21): p. 5301-5338.
30. Li, Q., et al., *Thiourethane-based thiol-ene high T-g networks: Preparation, thermal, mechanical, and physical properties.* J. Polym. Sci. Part A: Polym. Chem, 2007. **45**(22): p. 5103-5111.
31. Rosilo, H., et al., *Transition to Reinforced State by Percolating Domains of Intercalated Brush-Modified Cellulose Nanocrystals and Poly(butadiene) in Cross-Linked Composites Based on Thiol-ene Click Chemistry.* Biomacromolecules, 2013. **14**(5): p. 1547-1554.
32. Boyer, C., et al., *Modification of RAFT-Polymers via Thiol-Ene Reactions: A General Route to Functional Polymers and New Architectures.* J. Polym. Sci. Part A: Polym. Chem, 2009. **47**(15): p. 3773-3794.
33. Nilsson, C., et al., *Dendrimers in Thiol-ene Crosslinked Networks and the Effect of Subsequent Generations on Thermoset Properties.* J. Polym. Sci. Part A: Polym. Chem, 2009. **47**(2): p. 589-601.
34. Dondoni, A., *The Emergence of Thiol-Ene Coupling as a Click Process for Materials and Bioorganic Chemistry.* Angewandte Chemie-International Edition, 2008. **47**(47): p. 8995-8997.
35. Wei, H., et al., *Photopolymerization of ternary thiol-ene/acrylate systems: Film and network properties.* J. Polym. Sci. Part A: Polym. Chem, 2007. **45**(5): p. 822-829.
36. Senyurt, A.F., et al., *Physical and mechanical properties of photopolymerized thiol-ene/acrylates.* Macromolecules, 2006. **39**(19): p. 6315-6317.
37. Khire, V.S., T.Y. Lee, and C.N. Bowman, *Surface modification using thiol-acrylate conjugate addition reactions.* Macromolecules, 2007. **40**(16): p. 5669-5677.
38. Senyurt, A.F., et al., *Ternary thiol-ene/acrylate photopolymers: Effect of acrylate structure on mechanical properties.* Macromolecules, 2007. **40**(14): p. 4901-4909.
39. Kusuma, V.A., et al., *Crosslinked poly(ethylene oxide) containing siloxanes fabricated through thiol-ene photochemistry.* J. Polym. Sci. Part A: Polym. Chem, 2015. **53**(13): p. 1548-1557.

40. Mergy, J., et al., *Modification of polysaccharides via thiol-ene chemistry: A versatile route to functional biomaterials.* J. Polym. Sci. Part A: Polym. Chem, 2012. **50**(19): p. 4019-4028.
41. Kade, M.J., D.J. Burke, and C.J. Hawker, *The Power of Thiol-ene Chemistry.* J. Polym. Sci. Part A: Polym. Chem, 2010. **48**(4): p. 743-750.
42. Fringuelli, F. and A. Taticchi, *The Diels-Alder reaction: selected practical methods*2002: John Wiley & Sons.
43. Carruthers, W., *Cycloaddition reactions in organic synthesis*2013: Elsevier.
44. Kappe, C.O., S.S. Murphree, and A. Padwa, *Synthetic applications or furan Diels-Alder chemistry.* Tetrahedron, 1997. **53**(42): p. 14179-14233.
45. Gandini, A. and M.N. Belgacem, *Furans in polymer chemistry.* Progress in Polymer Science, 1997. **22**(6): p. 1203-1379.
46. Gheneim, R., C. Perez-Berumen, and A. Gandini, *Diels-Alder reactions with novel polymeric dienes and dienophiles: Synthesis of reversibly cross-linked elastomers.* Macromolecules, 2002. **35**(19): p. 7246-7253.
47. Laita, H., S. Boufi, and A. Gandini, *The application of the Diels-Alder reaction to polymers bearing furan moieties .1. Reactions with maleimides.* European Polymer Journal, 1997. **33**(8): p. 1203-1211.
48. Gousse, C., A. Gandini, and P. Hodge, *Application of the Diels-Alder reaction to polymers bearing furan moieties. 2. Diels-Alder and retro-Diels-Alder reactions involving furan rings in some styrene copolymers.* Macromolecules, 1998. **31**(2): p. 314-321.
49. Canary, S.A. and M.P. Stevens, *Thermally reversible cross-linking of polystyrene via the furan-maleimide diels-alder reaction.* J. Polym. Sci. Part A: Polym. Chem, 1992. **30**(8): p. 1755-1760.
50. Chujo, Y., K. Sada, and T. Saegusa, *A novel nonionic hydrogel from 2-methyl-2-oxazoline .4. reversible gelation of polyoxazoline by means of diels-alder reaction.* Macromolecules, 1990. **23**(10): p. 2636-2641.
51. Phillips, J.C., et al., *Short-term toxicity of furfuryl mercaptan in rats.* Food and Cosmetics Toxicology, 1977. **15**(5): p. 383-387.
52. Bétron, C., V. Bounor-Legaré, and P. Cassagnau, *Control of diffusion and exudation of vegetable oils in EPDM copolymers.* European polymer Journal submit, 2016: p. 26.
53. Neuburger, N.A. and B.E. Eichinger, *Critical experimental test of the Flory-Rehner theory of swelling.* Macromolecules, 1988. **21**(10): p. 3060-3070.
54. Chi, M.S., *Compatibility of cross-linked polymers with plasticizers by glass-transition temperature-measurement and swelling tests.* J. Polym. Sci. Part A: Polym. Chem, 1981. **19**(7): p. 1767-1779.
55. Flory, P.J., *Statistical mechanics of swelling of network structures.* Journal of Chemical Physics, 1950. **18**(1): p. 108-111.
56. Flory, P.J. and J. Rehner, *Statistical Mechanics of Cross-Linked Polymer Networks II. Swelling.* The Journal of Chemical Physics, 1943. **11**(11): p. 521-526.
57. Patel, S.K., et al., *Elastic modulus and equilibrium swelling of poly(dimethylsiloxane) networks.* Macromolecules, 1992. **25**(20): p. 5241-5251.
58. Sheehan, C.J. and A.L. Bisio, *Polymer/Solvent Interaction Parameters.* Rubber Chemistry and Technology, 1966. **39**(1): p. 149-192.
59. Peng, Z., et al., *Reinforcement of EPDM by in situ prepared zinc dimethacrylate.* Journal of Applied Polymer Science, 2002. **84**(7): p. 1339-1345.

60. Jose T, S. and J. Rani, *EPDM/CIIR Blends: Effect of EPDM Grade on Mechanical Properties.* International Journal of Polymeric Materials and Polymeric Biomaterials, 2007. **56**(7): p. 743-758.
61. El-Sabbagh, S.H., A.I. Hussain, and M.A.A. El-Ghaffar, *Utilisation of maleic anhydride and epoxidised soyabean oil as compatibilisers for NBR/EPDM blends reinforced with modified and unmodified polypropylene fibres.* Pigment & Resin Technology, 2005. **34**(4): p. 203-217.
62. Hrnjak-Murgić, Z., J. Jelenčić, and M. Bravar, *The role of molar volume of the organic solvents in the swelling system EPDM vulcanizate/solvent.* Die Angewandte Makromolekulare Chemie, 1996. **242**(1): p. 85-96.
63. Chen, J., et al., *Synthesis and application of a natural plasticizer based on cardanol for poly(vinyl chloride).* Journal of Applied Polymer Science, 2015. **132**(35): p. n/a-n/a.
64. Altenhofen da Silva, M., et al., *Polyvinylchloride (PVC) and natural rubber films plasticized with a natural polymeric plasticizer obtained through polyesterification of rice fatty acid.* Polymer Testing, 2011. **30**(5): p. 478-484.
65. *ASTM Standards, Designation D 395 (ISO 815) Standard Test Methods for Rubber Property-Compression Set*, 1989. p. 34-38.
66. Joubert, C., et al., *Influence of the crosslink network structure on stress-relaxation behavior: Viscoelastic modeling of the compression set experiment.* J. Polym. Sci. Part B: Polym. Physi, 2003. **41**(15): p. 1779-1790.
67. Posner, T., *Beiträge zur Kenntniss der ungesättigten Verbindungen. II. Ueber die Addition von Mercaptanen an ungesättigte Kohlenwasserstoffe.* Berichte der deutschen chemischen Gesellschaft, 1905. **38**(1): p. 646-657.
68. Silveira, C.C., S.R. Mendes, and F.M. Líbero, *Solvent-Free Anti-MarkovnikovAddition of Thiols to Alkenes Using Anhydrous Cerium (III) Chloride as Catalyst.* Synlett, 2010. **2010**(05): p. 790-792.
69. Wu, J.F., et al., *Synthesis of Soybean Oil-Based Thiol Oligomers.* ChemSusChem, 2011. **4**(8): p. 1135-1142.
70. Tyson, E.L., M.S. Ament, and T.P. Yoon, *Transition Metal Photoredox Catalysis of Radical Thiol-Ene Reactions.* Journal of Organic Chemistry, 2013. **78**(5): p. 2046-2050.
71. Shostakovskii, M.F., E. Gracheva, and N. Kul'bovskaya, *Methods of preparation and properties of substituted vinyl ethers and sulphides.* Russian Chemical Reviews, 1961. **30**(4): p. 207-219.
72. Cao, C., L.R. Fraser, and J.A. Love, *Rhodium-catalyzed alkyne hydrothiolation with aromatic and aliphatic thiols.* Journal of the American Chemical Society, 2005. **127**(50): p. 17614-17615.
73. Hoyle, C.E., T.Y. Lee, and T. Roper, *Thiol–enes: Chemistry of the past with promise for the future.* J. Polym. Sci. Part A: Polym. Chem, 2004. **42**(21): p. 5301-5338.
74. Dijkhuis, K.A.J., J.W.M. Noordermeer, and W.K. Dierkes, *The relationship between crosslink system, network structure and material properties of carbon black reinforced EPDM.* European Polymer Journal, 2009. **45**(11): p. 3302-3312.
75. Martin, G., et al., *Viscoelasticity of randomly crosslinked EPDM networks.* Polymer, 2008. **49**(7): p. 1892-1901.
76. Benson, S.W., *Thermochemistry and kinetics of sulfur-containing molecules and radicals.* Chemical Reviews, 1978. **78**(1): p. 23-35.
77. Mackle, H., *The thermochemistry of sulphur-containing molecules and radicals—II.* Tetrahedron, 1963. **19**(7): p. 1159-1170.

78. Luo, Y.-R., *Handbook of bond dissociation energies in organic compounds*2002: CRC press.

CHAPITRE IV:

Publication 4: “EPDM crosslinking from bio-based vegetable oil and alkoxysilane hydrolysis–condensation reactions”

EPDM crosslinking from bio-based vegetable oil and alkoxysilane hydrolysis–condensation reactions

Cyrille Bétron, Véronique Bounor-Legaré, Philippe Cassagnau

CNRS, UMR5223, Ingénierie des Matériaux Polymères, Université Lyon 1, 15, Bd. Latarjet, F-69622 Villeurbanne, cedex, France

Abstract

The aim of this study is to design a process of plasticization and crosslinking of an EPDM matrix with a thioalkoxysilane coupling agent. For this purpose, we used a highly reactive vegetable oil, tung oil, composed of around 80 wt% α-eleostearic acid. Owing to the low compatibility and weak interaction between the vegetable oil and the EPDM matrix, we had to use a di-functional compatibilizing agent, 3-mercaptopropyltriethoxysilane. This alkoxysilane was successfully grafted onto the tung oil and the EPDM matrix, and also allowed the crosslinking of the matrix and the vegetable oil through alkoxysilane hydrolysis–condensation reactions. The grafting reaction was analyzed by liquid ^{1}H NMR spectroscopy. The crosslinked sample was characterized by different mechanical tests, and the morphology by SEM. These results are compared with an EPDM sample crosslinked by dicumyl peroxide (DCP) and plasticized by a mineral oil.

Keywords: EPDM, tung oil, standoil, homopolymerization, thiol-ene, 3-mercaptopropyltriethoxysilane, hydrolysis-condensation, alkoxysilane.

I- Introduction

Crosslinking is one of the most important methods for extending the useful range of commodity polymers to meet the high demands of special applications. In addition to conventional peroxide crosslinking or irradiation crosslinking, the use of alkoxysilane–water crosslinking has gained considerable attention in recent years. This concerns not only its industrial applications, such as cable insulation and water heating pipes [1], but also fundamental research [2-7], because of its various advantages, such as easy processing, low capital investment, and favorable properties of the crosslinked materials. Alkoxysilane–water crosslinking is one of the well-known techniques used in crosslinking polyethylene (PE) [2-4, 8-13]. It can also be used in the crosslinking of ethylene copolymer [14-18], polypropylene (PP) [19-22], polyvinyl chloride [23, 24], rubber [1, 25, 26], etc. These crosslinking agents present two functional groups, an organofunctional and a silicofunctional group, the latter preferably being an alkoxysilane group. The organofunctional group, bonded via a short alkyl chain to the silicon atom, can be of a highly diversified nature, such as –SH, $–NH_2$, $–CH=CH_2$, SO_2N_3, etc., and can react with the polymer during the curing process [27, 28]. Subsequently, the alkoxysilane-grafted polymer is crosslinked by exposure to a humid environment. The crosslinking reaction involves the hydrolysis of alkoxysilane groups with moisture, followed by condensation of the formed hydroxyl groups to create stable siloxane linkages [29]. Many studies have explored the use of alkoxysilanes as a coupling agent between the filler and the rubber [30-36], but seldom as a cross-linking agent. Nevertheless, we can cite some work: for example, Gonzalez et al. [37] used an azide sulfonyl alkoxysilane as a coupling agent able to be grafted onto saturated or unsaturated rubber. After these grafting steps, the coupling agent allowed the crosslinking of the rubber by hydrolysis–condensation of the alkoxysilane functions. This study was notable for proposing an organofunctional group able to be grafted onto any polymer with a CH function. Liu et al. [38] studied the crosslinking of PP by grafting methacryloylpropyltrimethoxysilane and vinyltriethoxysilane in a batch mixer and curing in hot water. Another method was used by Lai et al. [39], who grafted vinyltriethoxysilane onto the matrix by a radical reaction, using a peroxide agent and crosslinking the materials by condensation reactions. The reaction between vegetable oil and 3-mercaptopropyltrimethoxysilane via thiol–ene coupling was previously studied by Fu et al. [40], who described a novel method to obtain a bio-based material with hydrophobic characteristics. The 3-mercaptopropyltrimethoxysilane was coupled with castor oil by photochemistry, in which the monomer was polymerized with

isophorone diisocyanate. The material obtained was crosslinked by hydrolysis–condensation reactions to obtain bio-based polyurethane/siloxane with hydrophobic characteristics. This work highlighted the possibility of using the thiol–ene reactivity of the double bonds in natural oils and of crosslinking the material obtained by the hydrolysis–condensation reaction of an alkoxysilane.

The aim of the present work is to crosslink a synthetic rubber with a di-functional molecule, 3-mercaptopropyltriethoxysilane, by a thiol–ene reaction between the rubber and a vegetable oil activated by thermal treatment. The final step of the hydrolysis–condensation reaction, without using any catalyst, was achieved to completely crosslink the system. The obtained sample was also compared with a similar sample, crosslinked with a peroxide agent, in terms of viscoelastic behaviors and mechanical properties.

II- Experimental

II-1) Materials and samples

The EPDM used was a Vistalon® 8600 (ExxonMobilChemical) kindly supplied by Hutchinson. Its chemical structure was determined by liquid ^{1}H NMR spectroscopy (Fig. 1). At 7.0 ppm, we observed a signal corresponding to the proton resonance of aromatic groups due to the presence of oil. The signal between 5.38 and 5.13 ppm was attributed to the proton resonance from the –C**H**= on the norbornene repetitive units. The Vistalon functionality corresponds to 0.74 mmol of diene per gram of EPDM. The average molar mass values M_n = 69,000 g·mol^{-1} and M_w = 203,000 g·mol^{-1} were measured by size exclusion chromatography. Its density is ρ = 870 kg·m^{-3} and its Mooney viscosity ML (1+8 at 125°C) is 81 MU based on test ASTM D1646. The solubility parameters are δ_D = 18.29 MPa$^{1/2}$, δ_P = 1.91 MPa$^{1/2}$, δ_H = 2.03 MPa$^{1/2}$ for a global solubility parameter δ_{tot} = 18.5 MPa$^{1/2}$.

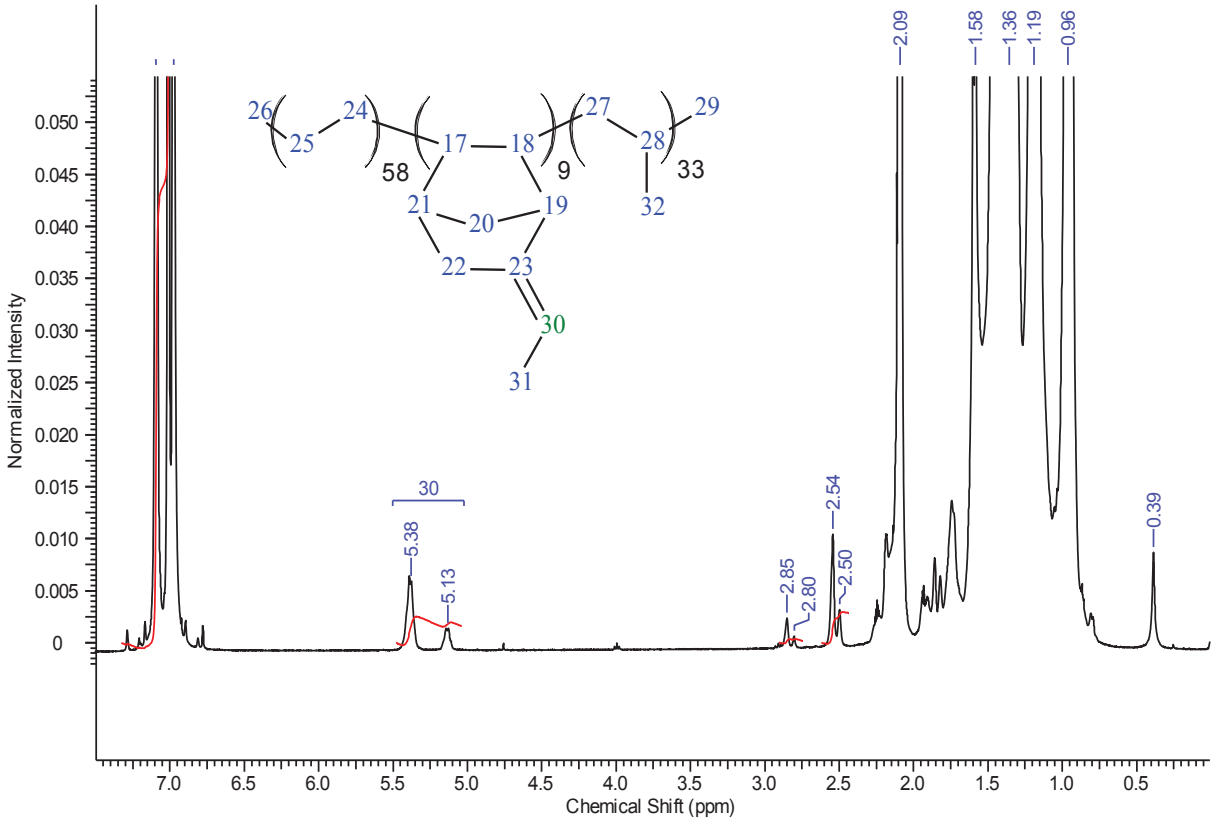


Fig. 1. Liquid ^{1}H NMR spectrum of EPDM Vistalon 8600 (toluene d8)

3-Mercaptopropyltriethoxysilane (3-MTS) with a purity of 92%, supplied by ABCR, was analyzed by liquid ^{1}H NMR as shown in Fig. 2. Its boiling temperature is 210°C, with a molar mass of 238.42 g·mol^{-1} and a density of 0.987 g·mL^{-1} at 25°C. The solubility parameters are δ_D = 15.2 MPa$^{1/2}$, δ_P = 4.0 MPa$^{1/2}$, δ_H = 3.8 MPa$^{1/2}$ for a global solubility parameter δ_{tot} = 16.2 MPa$^{1/2}$, corresponding to a relative energy difference (RED) with the EPDM matrix of 0.94. This value is considered in theory as the limit of compatibility [41, 42].

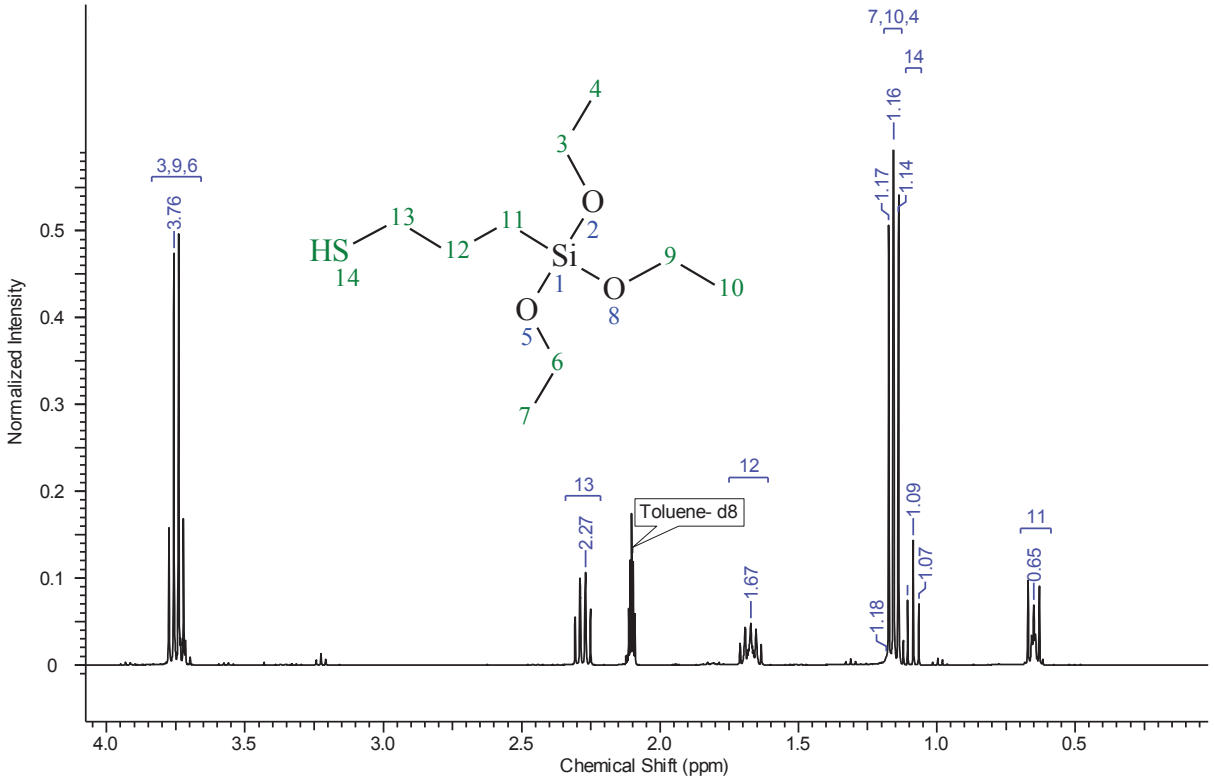


Fig. 2. Liquid ^{1}H NMR spectrum of 3-mercaptopropyltriethoxysilane (toluene D-8 at 30°C)

Two oils were used in this study. Torilis® 7200 was used as a reference. The specific gravity of this oil is 0.90 g·cm^{-3} at 20°C. The solubility parameters are δ_D = 19.8 MPa$^{1/2}$, δ_P = 0.8 MPa$^{1/2}$, δ_H = 5.0 MPa$^{1/2}$ for a global solubility parameter δ_{tot} = 20.5 MPa$^{1/2}$. It is a commercial mineral oil commonly used for EPDM plasticization. The second one is tung oil supplied by Sigma-Aldrich. This is a vegetable oil used as a very reactive plasticizer. Its chemical structure was determined by ^{1}H NMR (Fig. 3). The specific gravity of this oil is 0.937 g·cm^{-3} at 20°C. The solubility parameters are δ_D = 16.7 MPa$^{1/2}$, δ_P = 5.7 MPa$^{1/2}$, δ_H = 5.8 MPa$^{1/2}$ for a global solubility parameter δ_{tot} = 18.5 MPa$^{1/2}$. The compatibility with the EPDM matrix was studied in previous work [43].

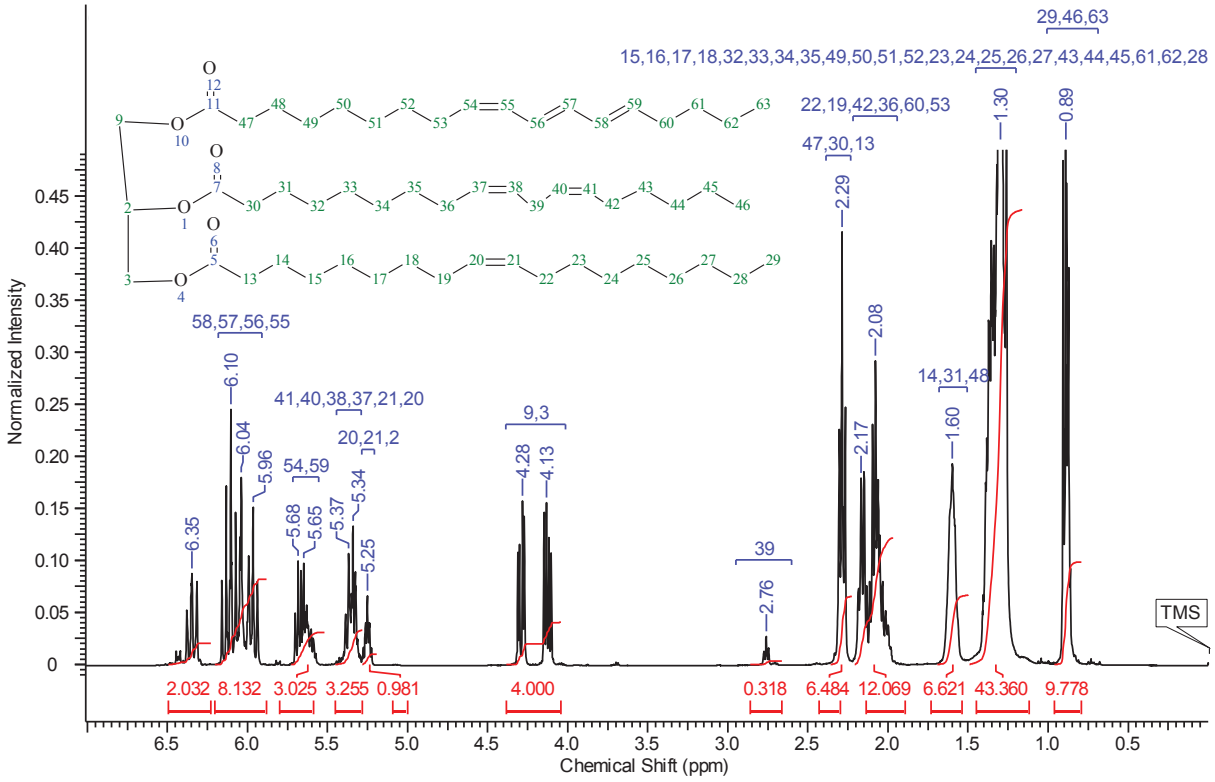


Fig. 3. Liquid ^{1}H NMR spectrum of Tung oil (toluene d-8 at 30°C).

Finally, dicumyl peroxide (DCP) with a purity of 98% was supplied by Sigma-Aldrich and was used as a reference for comparison to crosslink the EPDM sample.

II-2) Sample preparation

The EPDM samples crosslinked by DCP were prepared in an internal batch mixer (Haake Rheomix 50 cm^3) at 50 rpm and at a temperature of 80°C to avoid activating radical reactions during mixing. The following protocol was adopted: First, 30 g of EPDM (22.2 mmol of diene) and 0.5 wt% (0.9 mmol) or 1 wt% (1.8 mmol) of crosslinking agents were introduced into the cavity and mixed for 5 min in order to ensure thermal homogenization. In the second step, 30 wt% of Torilis® 7200 plasticizer was introduced and mixed until complete homogenization. Then, all samples were compression-molded into 1 mm-thick sheets at 180°C for 10 min to activate the DCP decomposition and the crosslinking reactions.

The EPDM samples crosslinked with the 3-MTS were prepared using the same method. 15 mL of 3-MTS (57.2 mmol), corresponding to a consumption of 34% of the global diene functions (EPDM and tung oil double bonds), was mixed with 30 g of EPDM for 10 min at 150°C. Then, in the second step, 30 wt% of tung oil (142.5 mmol of unsaturated groups) was introduced and mixed until complete homogenization. Finally, the mixture was heated for 5 min at 250°C to consume the residual unsaturated groups, and the samples were compression-

molded into 1 mm-thick sheets at 150°C. This sample will be referred to as 3-MTS M. The sample 3-MTS M was then immersed in water at 80°C at pH = 2 for 6 h in order to optimize the hydrolysis reaction. After this step the sample will be referred to as 3-MTS H. Finally, the 3-MTS H sample was placed in a vacuum at 80°C for 2 h in order to enhance the condensation reaction; this sample will be referred to as 3-MTS HC. The names of all samples and the corresponding processing steps are summarized in Table 1.

Table 1. Description of the samples

Name of samples	Description
DCP-0.5%	EPDM reference sample crosslinked with 0.5% of DCP
DCP-1.0%	EPDM reference sample crosslinked with 1.0% of DCP
3-MTS M	After mixing with 3-MTS, before hydrolysis
3-MTS H	After mixing with 3-MTS, after hydrolysis
3-MTS HC	After mixing with 3-MTS, after condensation

II-3) Methods of characterization

- ***Liquid ^{1}H NMR***

The liquid ^{1}H NMR spectra were measured on a Bruker 400 Avance III (5 mm) with BBFO+ probe at a frequency of 400 MHz at 30°C. 25 mg of the samples was either solubilized or swollen in 1 ml of toluene-d8, and TMS was used as a reference.

- ***Rheological measurements***

Low-deformation rheological analyses were performed on an ARES 4800 with a parallel plate geometry (diameter 25 mm). Discs were cut into sample plates obtained after molding at 160°C.

Firstly, samples were submitted to a strain sweep test at 160°C, at a frequency of 10 rad·s^{-1}, from 0.01% to 30%, in order to determine the linear domain. Secondly, a time sweep test was carried out at 160°C, at a frequency of 10 rad·s^{-1}, and a strain corresponding to the linear domain in order to check that the sample rheology did not evolve during the time of the analysis. Finally, dynamic frequency sweep tests were performed at 160°C, at a strain of 1% corresponding to the linear domain, from 100 to 0.01 rad·s^{-1}.

- ***Swelling test***

Swelling experiments were carried out by immerging the EPDM-based sample in toluene. The system was allowed to reach equilibrium, and then the amount of solvent absorbed by the sample was measured using gravimetric or volumetric methods. The sample was then rinsed and dried. The non-crosslinked polymer chains were extracted and the sample weight was measured [44-46]. The insoluble fraction and amount of swelling are defined to determine the crosslinking density by the equation:

$$Q = \frac{V_s}{V_i} \quad (1)$$

where Q is the coefficient of swelling, V_s is the swelling volume and V_i is the initial volume before the swelling experiment. This equation can be rewritten as

$$Q = \frac{\frac{m_s}{\rho_s} + \frac{m_p}{\rho_p}}{\frac{m_p}{\rho_p}} \quad (2)$$

where m_s is the mass of toluene absorbed by the EPDM and $\rho_s = 867\ \mathrm{kg.m^{-3}}$ is the density of toluene, m_p the mass of the EPDM sample and $\rho_p = 860\mathrm{kg.m^{-3}}$ its density.

From the equilibrium swelling theory of Flory and Rehner [47], the crosslinking density υ can be calculated and expressed in $\mathrm{mol \cdot m^{-3}}$ [48]:

$$\upsilon = -\frac{ln(1-v_p)+v_p+\chi v_p^2}{V_{ms}\left(v_p^{1/3}-\frac{v_p}{2}\right)} \quad (3)$$

where $V_{ms} = 106.26\ \mathrm{ml \cdot mol^{-1}}$ is the molar volume of solvent, v_p is the volume fraction of EPDM in the swollen mass (i.e., the inverse of the swelling rate, $1/Q$), and χ is the interaction parameter between the polymer and solvent, sometimes referred to as the Flory–Huggins interaction parameter. In the present work we used $\chi = 0.49$, as generally assumed in the literature [49-53]. For the calculation of the insoluble fraction, the EPDM, the reagent and the vegetable oil will all be accounted for, because all these compounds are able to react during the heat treatment.

- ***Exudation test***

To measure the extent of exudation, the sample mass was measured, and the sample was then placed in an oven at 80°C for 7 days. The sample was then wiped with absorbent paper in order to remove excess oil from the surface. The mass difference allowed us to define the oil loss by exudation [54, 55].

- ***Compression set measurements***

Compression set testing [56] is used to determine the ability of elastomeric materials to maintain elastic properties after prolonged compressive stress. The test measures the permanent deformation of the specimen after it has been exposed to compressive stress for a set time period. A small cylinder of the crosslinked EPDM sample was placed between the parallel plates of the DMA (DMA Q800, TA Instruments, with compression modulus) and reheated to 100°C. The shape of the cylinder (radius R = 5 mm and thickness e = 2 mm (I_0)) was rigorously elaborated and size-controlled. The software was programmed to impose a nominal deformation of $\varepsilon_{0,n} = 0.25$ (I_1) for 24 h at 100°C.

After this loading time, the sample was removed from the plates and cooled to room temperature by placing it on a surface with poor thermal conduction properties for 30 min before measuring the final thickness (I_2). The compression set is expressed as a percentage of the original deflection, DRC [57]:

$$DRC = \frac{I_0 - I_1}{I_0 - I_2} * 100 \text{ with } \varepsilon_{0,n} = \frac{I_0 - I_2}{I_0} \quad (4)$$

- ***Tensile test***

Tensile tests were carried out using normalized dumb-bell-shaped samples of type H2. The tests were performed using a tensile-testing machine, with a crosshead speed of 500 mm·min^{-1}, at 20°C and 50% relative humidity. At least five specimens were tested for each EPDM formulation.

III- Results and discussion

As described in the introduction, the aim of this study is to carry out successively a thiol–ene reaction in an EPDM/tung oil system followed by hydrolysis–condensation reactions of the grafted alkoxysilane groups in order to develop a new method to crosslink EPDM. In that framework, we first described the expected reactions and characterized them under EPDM processing conditions. A specific comparison with the classical EPDM

crosslinking by DCP was detailed to illustrate the advantages of our new system. Following that, several tests were carried out to evaluate the crosslinking density, the compression set and the mechanical properties.

III-1) Grafting of 3-MTS onto EPDM/tung oil under dynamic conditions

The thiol–ene reaction is a well-known reaction. The addition of a thiol to an olefin was shown by Posner in 1905 [58]. Thiol–ene reactions involve the addition of a S-H bond to a double or triple bond by either a metal-catalyzed complexation [59] or free radical mechanism [60-62]. Thiol–ene reactions are essentially the sulfur version of the hydrosilylation reaction. Since these reactions are efficient, high-yielding, and tolerant to various solvents and functional groups, many researchers now consider the thiol–ene reaction as a "click" reaction.

In the present work, this reaction is expected to occur between the unsaturated groups of the norbornene moiety from the EPDM polymer matrix and the 3-MTS (Fig. 4). The experiment was carried out at 150°C in the internal mixer. We have to mention that at high temperatures (> 120°C), as demonstrated by Shostakovsky et al. [63] in 1961, this reaction is poorly selective [64]. However, this reaction remains interesting for grafting the 3-MTS reactive agent onto tung oil, and onto the norbornene function present on the EPDM. Moreover, in the work of Hoyle et al. [65], it has been noted that the norbornene function is one of the most reactive functions in the thiol–ene reaction.

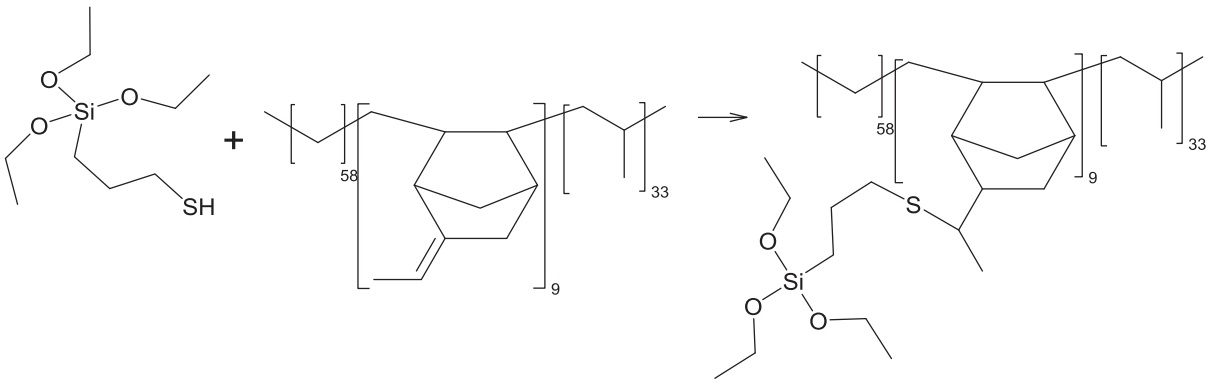


Fig. 4. Thiol-ene reaction on EPDM double bond

In the second step, 30 wt% of tung oil is introduced into the internal mixer at the same temperature. The mixture is stirred for a few minutes until complete incorporation of the vegetable oil. During the incorporation, the residual 3-MTS can be grafted onto the tung oil

double bond as shown in Fig. 5. This reaction has already been successfully carried out in similar conditions in previous work [66].

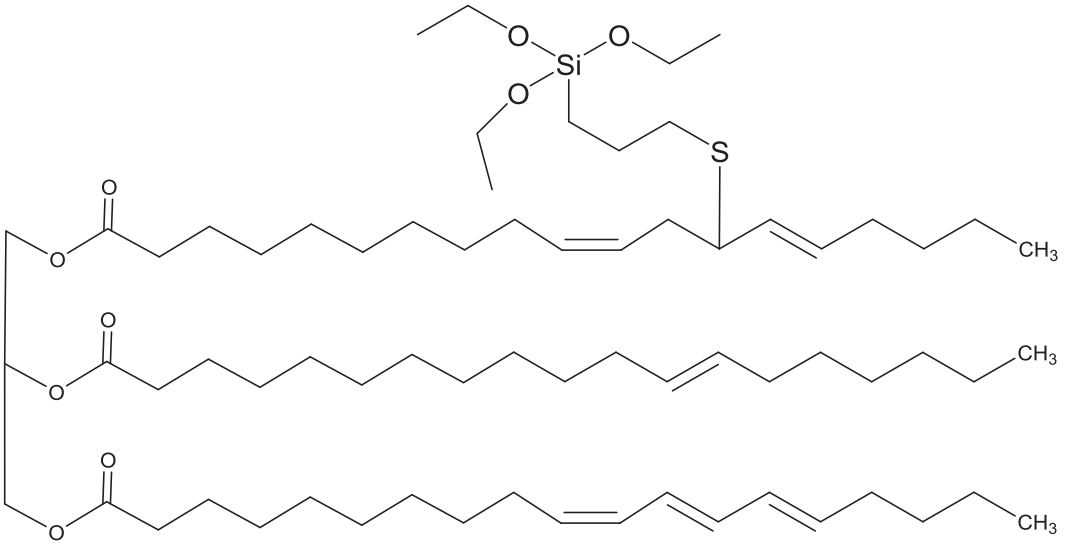


Fig. 5. Thiol-ene reaction between the Tung oil fatty acid and the 3-MTS

Finally, the reactional medium is heated up to 250–260°C in order to consume a part of the residual double bonds. In this range of temperature, the standoil reaction of the tung oil can be enhanced. This intra-molecular homopolymerization of the tung oil is used to create covalent bonds within the vegetable oil (Fig. 6). Based on our previous work [43], these reactions are expected to contribute to the densification of the crosslinking network.

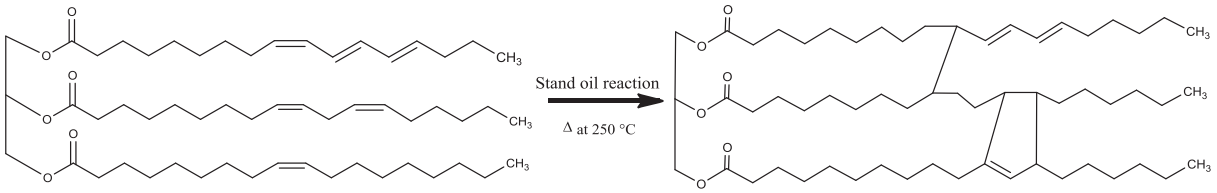


Fig. 6. Stand oil reaction on Tung oil [43]

At this step, the majority of thiol functions are grafted onto the double bonds present in the reactional medium. We obtained a 3-MTS M sample with a chemical structure similar to the illustration in Fig. 7.

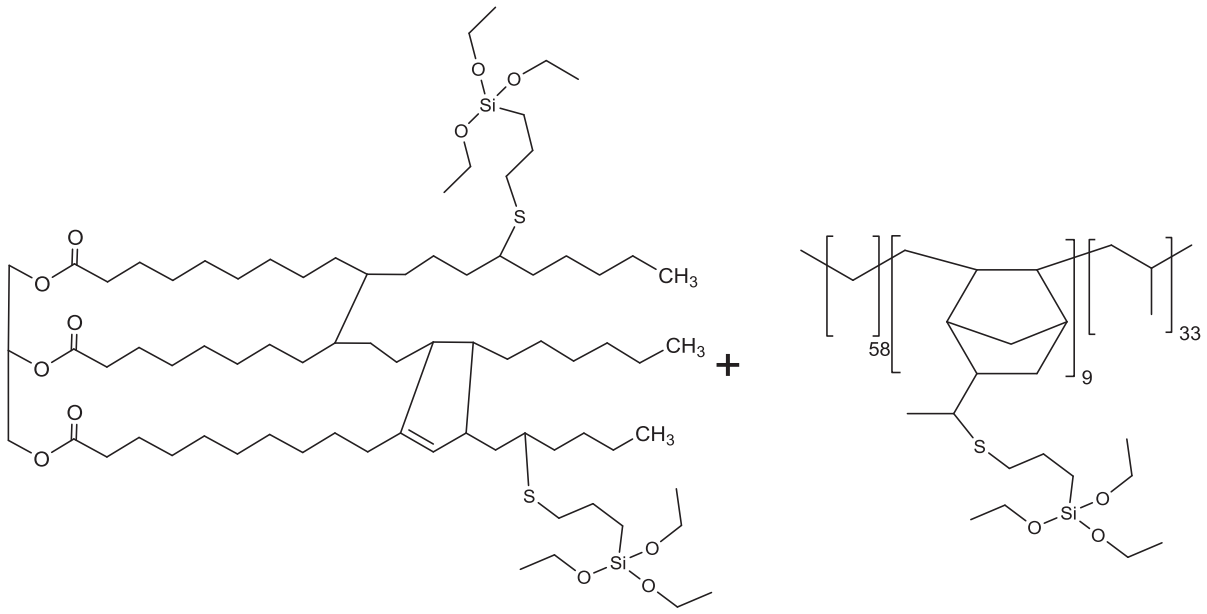


Fig. 7. Structure of 3-MTS M sample

The variation of the torque versus time during the reaction carried out in the internal mixer (Fig. 8) allows us first to qualitatively evaluate the efficiency of the expected reactions.

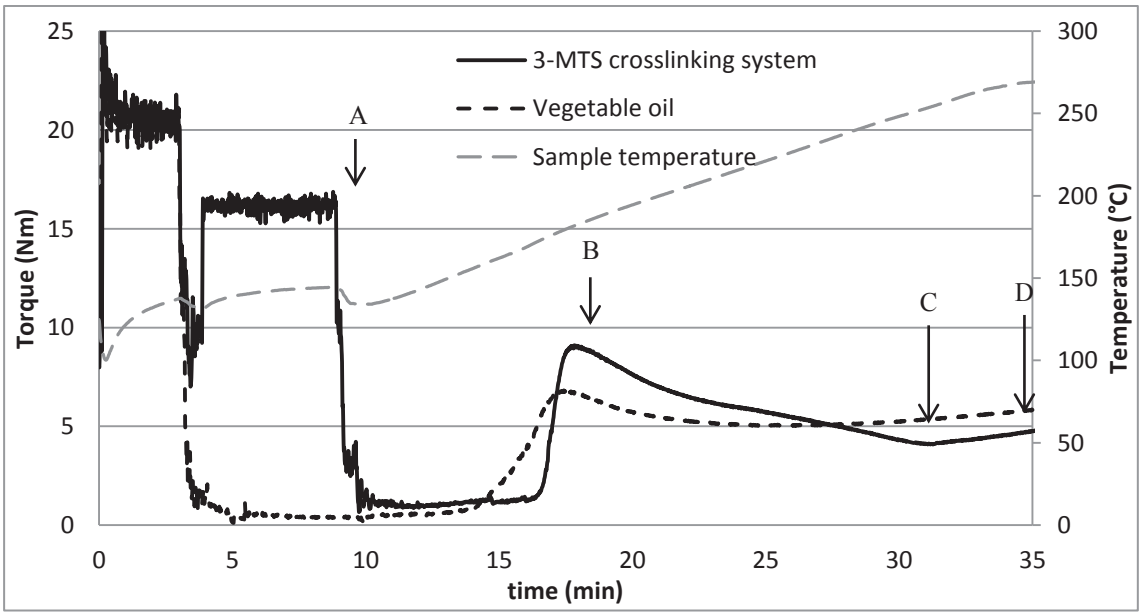


Fig. 8. Torque (Nm) and temperature (°C) evolutions versus time (min) during EPDM crosslinking reaction in an internal mixer with the 3-MTS (solid line) and without the 3-MTS (dotted line).

Different behaviors can be observed from these curves. At t = 0 min the EPDM matrix is introduced into the internal blender at 150°C and stirred for 3 min. At t = 3 min, 15 ml of 3-MTS is added (solid line), which corresponds to a large excess of thiol compared with the norbornene functions, with the norbornene having a molar ratio of 1/3 of the global diene

functions (tung oil and EPDM unsaturated groups). To graft a part of the 3-MTS onto the EPDM matrix, the formulation is stirred for 5 min at 150°C. The torque remains constant, around 16 Nm. At t = 10 min (point A on the curve), 30 wt% of tung oil is injected and the temperature is increased up to 250°C. During this stage, the phenomenon of lubrication leads to a decrease of the torque down to 0 Nm until the oil has penetrated the EPDM matrix. The significant increase of the torque up to 9 Nm, observed at 17 min (point B on the curve), corresponds to the complete diffusion of the vegetable oil in the EPDM matrix. The decrease of the torque between t = 18 min and t = 30 min (points B and C) is the result of the homogenization effect of the plasticizer, and of the increase of the temperature. At t = 30 min (point C), the critical temperature of 250°C is reached and the standoil reaction described previously begins. In this last step, we observe a slight increase of the torque between points C and D on the curve, similar to the dotted line. The dotted line on Fig. 8 represents the system without 3-MTS reagent, which is composed of the EPDM matrix and tung oil, and has already been studied in previous work on vegetable oil plasticization and standoil [43]. At t = 3 min, 30 wt% tung oil is added, leading to the same phenomenon as the one observed in the previous case. The time of penetration of the tung oil into the EPDM matrix is about 15 min, whereas it was around 8 min in the previous case. Thus the time of penetration is considerably reduced with the presence of the 3-MTS, suggesting that the 3-MTS acts as a compatibilizing agent. At t = 30 min and T = 250°C, no significant increase of the torque is observed, similarly to the system with 3-MTS. These results seem to confirm that the crosslinking reaction is not effective in these processing conditions, but the significant increase of the torque at 250°C could correspond to a standoil reaction.

The sample 3-MTS M was analyzed with the swelling test after mixing (point D on Fig. 8). No insoluble fraction is observed, which demonstrates that the hydrolysis and condensation reactions are not sufficient for the establishment of a crosslinking network. The exudation test shows a substantial mass loss of 28%, and confirms the necessity of crosslinking the sample in order to stabilize it.

The chemical structure of the 3-MTS M sample after mixing was elucidated by liquid ^{1}H NMR spectroscopy (Fig. **9**). We focused especially on the following spectral zones:

- At 3.00–3.45–3.50 ppm, signals corresponding to the proton resonance from the –S-C**H** group in the α-position of the –S for the thiol–ene reaction.

- At 3.31 ppm, signals corresponding to the proton resonance from the CH_3-C**H**$_2$-OH group of the ethanol function after the partial hydrolysis reaction.

- At 3.75 ppm, signals corresponding to the proton resonance from the Si-O-C**H**$_2$ group of the ethoxy function.

- Around 5.0–5.5 ppm, signals corresponding to proton resonance from the norbornene double bond group for the thiol–ene reaction and mono-unsaturated groups from the fatty acid.

- Around 5.5–6.25 ppm, signals corresponding to the proton resonance from the conjugated double bond from the tung oil for the Diels–Alder reaction and other contributing radical reactions.

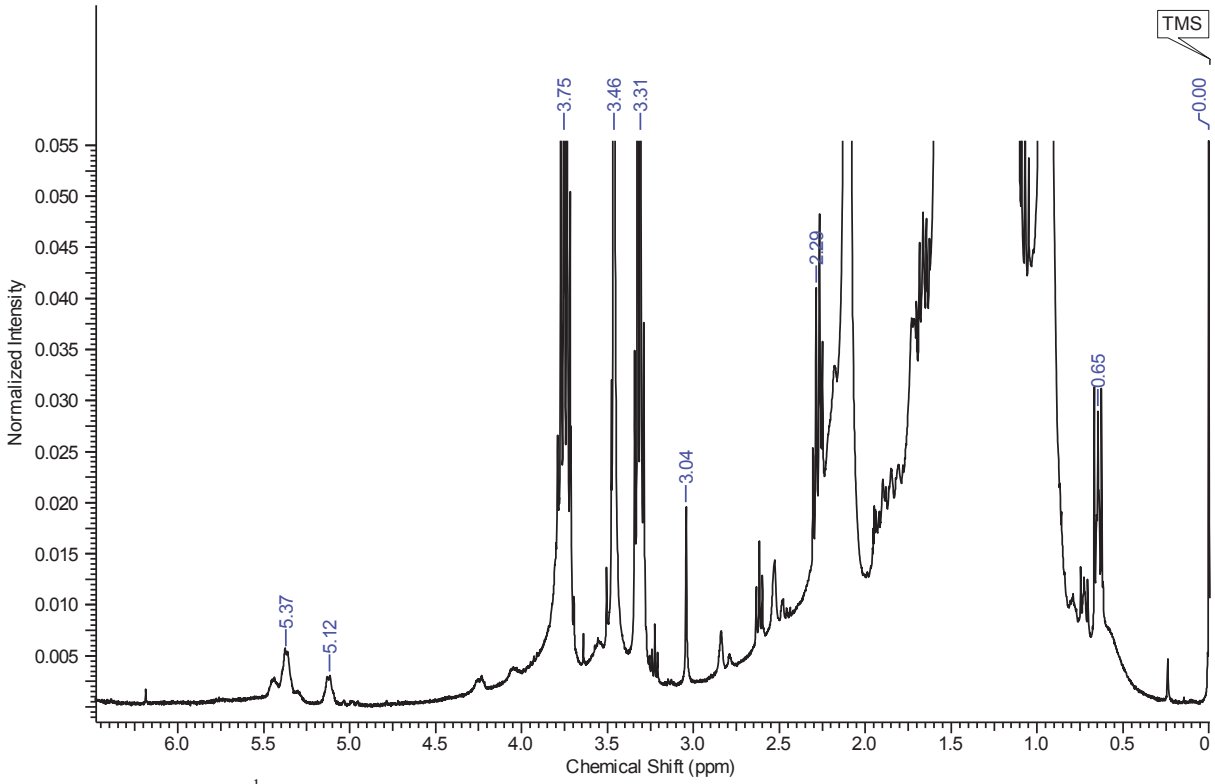


Fig. 9. Liquid ^{1}H NMR spectrum of 3-MTS M sample, center between 0.0 and 6.25 ppm (toluene d-8 at 30°C).

The signals at 3.04 and 3.46 ppm confirm the grafting of the thiol function onto the double bonds. The signal at 3.31 ppm shows a partial hydrolysis reaction, and the signal at 3.75 ppm is due to the presence of the non-hydrolyzed 3-MTS. If we focus on the signals at 5.12 and 5.37 ppm, we notice that the mono-unsaturated groups of the vegetable oil and the norbornene double bond are not completely consumed. Between 5.50 and 6.25 ppm the proton signals

corresponding to the vegetable oil poly-unsaturated groups are absent, confirming their consumption by the grafting and standoil reactions.

III-2) Hydrolysis–condensation reactions

As mentioned before, the 3-MTS M samples obtained after internal mixing are not crosslinked: the 3-MTS product was only grafted onto the tung oil and the EPDM matrix. To further crosslink this system, hydrolysis–condensation reactions of alkoxysilane were carried out, as represented in Fig. 10.

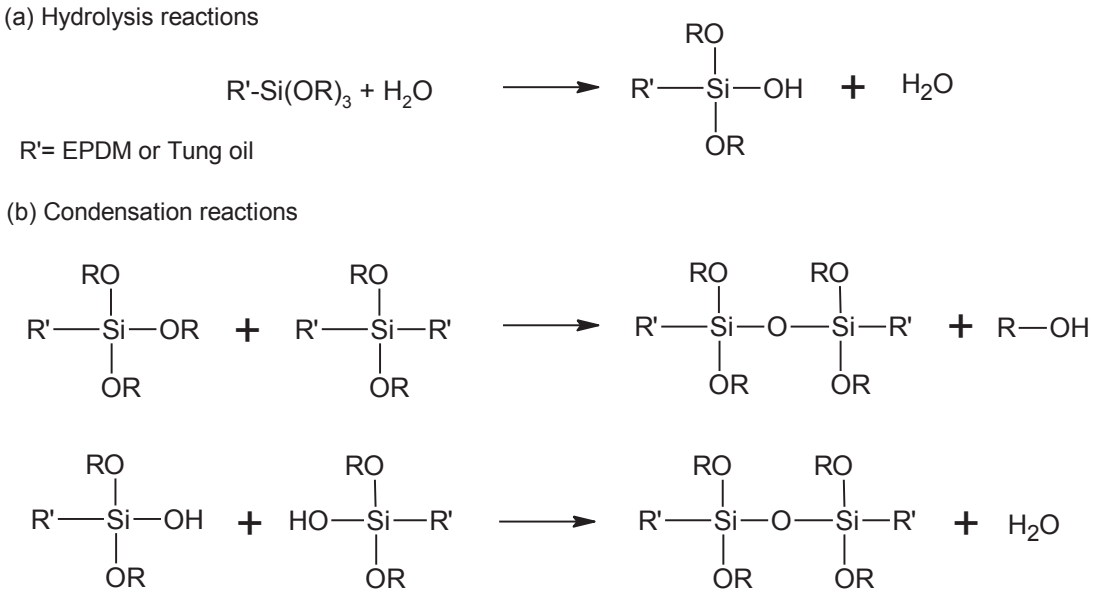


Fig. 10. Schematic reaction of hydrolysis-condensation reaction.

To optimize these reactions, the 3-MTS M sample was immersed in water, as described in the experimental part to obtain the 3-MTS H. Then, the 3-MTS H sample was analyzed by the swelling test, and an insoluble fraction of 27 ± 3 wt% was obtained, for a swelling ratio of 17.7 and a density of crosslinking of 2.3 ± 0.1 mol·m^{-3}. This indicated the poor reactivity of this system in such conditions. The exudation test showed a mass loss of 16%, which is better than that of the 3-MTS M sample, but still indicates that the condensation reactions were not sufficiently enhanced.

The chemical structure of the 3-MTS H sample (where the soluble part is 70 wt%) swollen in deuterated toluene was elucidated by liquid ^{1}H NMR spectroscopy (Fig. **11**).

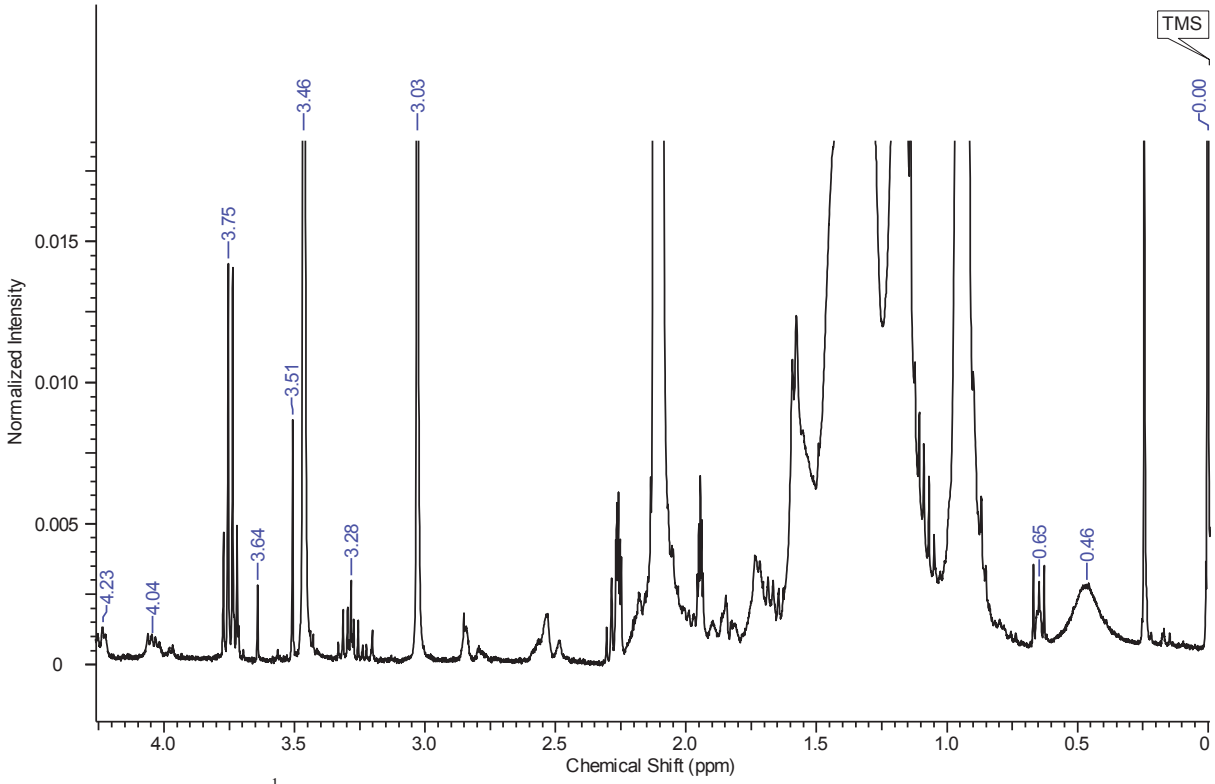


Fig. 11. Liquid ^{1}H NMR spectrum of 3-MTS H sample, center between 0.0 and 4.25 ppm (toluene d-8 at 30°C).

At 0.46 and 0.65 ppm, we observe a chemical shift of the signals corresponding to the proton resonance from the Si-C**H**$_2$-CH$_2$- group, a shift potentially due to a partial condensation reaction. We can deduce that 62 mol% of the 3-MTS is partially or totally condensed. The signal at 3.28 ppm shows a residual ethanol function, and the signal at 3.75 ppm, corresponding to the non-hydrolyzed ethoxy groups, allow us to calculate a hydrolysis percentage of about 80 mol% of the ethoxy functions compared with the 3-MTS M sample. These results confirm the hydrolysis reaction of the 3-MTS H sample and a partial condensation of these species. Furthermore, the hydrolysis results observed are similar to the work of Salon [67] on the kinetic hydrolysis of 3-mercaptopropyltrimethoxysilane and 3-aminopropyltriethoxysilane. On the other hand, the swelling test seems to indicate that the condensation reaction is not completed.

A further thermal treatment was applied to the 3-MTS H sample, as described in the experimental part, in order to enhance the condensation reactions.

The 3-MTS HC sample was analyzed by the swelling test, and an insoluble fraction of 92 $\pm$ 2 wt% was determined, for a swelling ratio of 13.0 and a density of crosslinking of 5.0

$\pm$ 0.1 mol·m^{-3}. This confirms the efficiency of the condensation reaction. The exudation test shows a mass loss of 2%. The 3-MTS HC sample seems to be stable over time.

The chemical structure of the system (of which the soluble part is 10 wt%) of the 3-MTS HC sample swollen in deuterated toluene was elucidated by liquid ^{1}H NMR spectroscopy (Fig. 12).

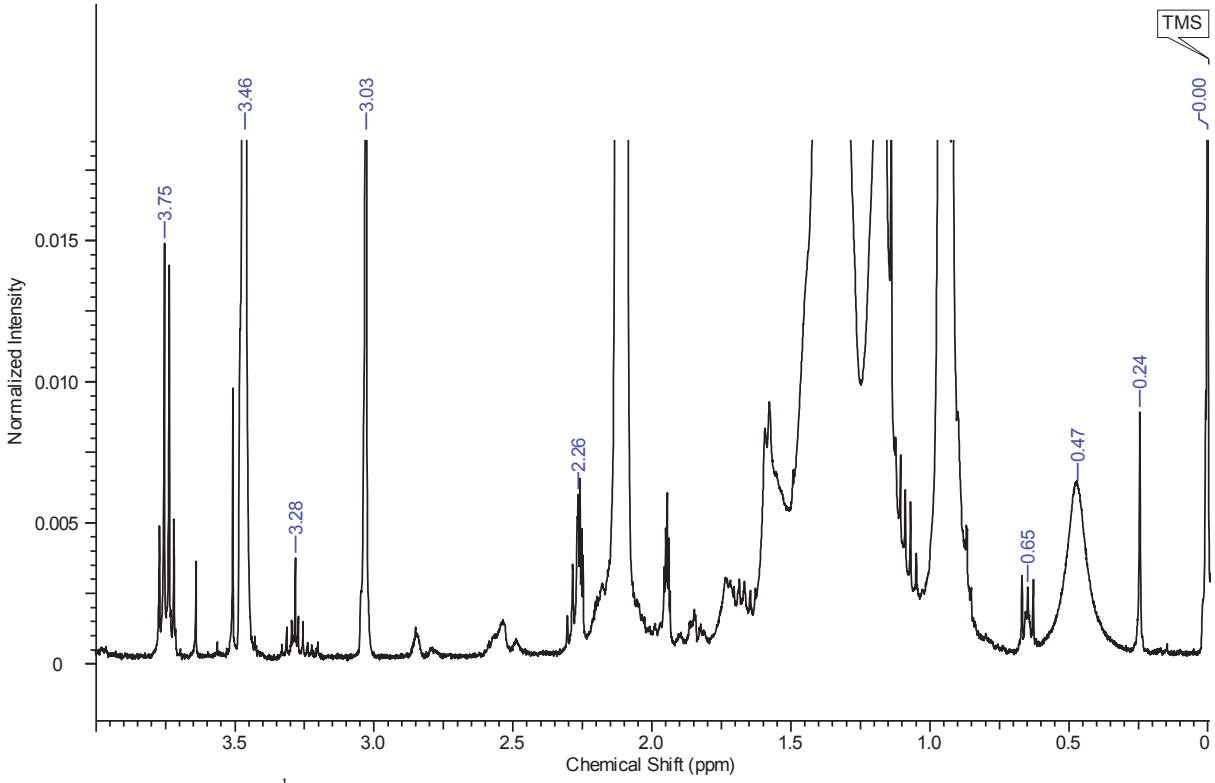


Fig. 12. Liquid ^{1}H NMR spectrum of the 3-MTS HC sample swollen in deuterated toluene, center between 0.0 and 4.00 ppm (toluene d-8 at 30°C).

At 0.46–0.65 ppm, we observe an increase of the intensity of the chemical shift corresponding to the proton resonance from the Si-C**H**$_2$-CH$_2$- group. We can deduce that in the 3-MTS HC sample, 89 mol% of 3-MTS is partially or totally condensed. The signal at 3.75 ppm allows us to calculate a hydrolysis percentage of about 85 mol% of the ethoxy functions in this solution compared with the 3-MTS M sample. The signals at 3.03, 3.46 and 3.51 ppm show an increase of 50 mol% of the grafting compared with the 3-MTS M sample. These results confirm the efficiency of the condensation reaction, and the swelling test seems to indicate that the condensation reactions allow the creation of crosslinking nodes.

III-3) 3-MTS versus classical peroxide crosslinking

In this part, the characteristics of the samples crosslinked with 3-MTS and the one crosslinked by DCP, classically used for the EPDM matrix, are compared. The sample 3-MTS

HC was analyzed and compared with reference EPDM samples formulated with the same quantities of mineral oil and crosslinked by radical reactions with 0.5 wt% and 1.0 wt% of DCP.

- ***Determination of the crosslinking density and viscoelastic behavior***

From the swelling experiments, the insoluble fraction and the crosslinking densities were determined and compared (Table 2).

Table 2. Swelling results for different EPDM formulation with 3-MTS crosslinking and radical crosslinking

Materials	Insoluble %	υ_p	Q=1/υ_p	υ mol/m^3
DCP-0.5%	50±2	0.02	46	0.3±0.1
DCP-1.0%	64±2	0.05	22	1.3±0.1
3-MTS HC	92±2	0.08	13	5.0±0.1

Compared with the 3-MTS HC sample, the reference samples based on DCP crosslinking displayed lower insoluble fractions, with 50% for 0.5 wt% of DCP and 64% for 1.0 wt% of DCP, compared with the 92% obtained with the 3-MTS system. Similarly, the swelling ratios are higher: 46 for 0.5 wt% of DCP and 22 for 1.0 wt% of DCP. The υ values are also markedly different, with a low crosslinking density of around 0.3 mol·m^{-3} for 0.5 wt% of DCP and 1.3 mol·m^{-3} for 1.0 wt% of DCP. In contrast, the υ value for the 3-MTS HC sample is 5.0 mol·m^{-3}, which shows a higher network density. Our system is consistent, for example, with the system studied by Sen et al. [5], based on vinyltriethoxysilane grafted onto PE and EPR, and crosslinked by a condensation reaction of an alkoxysilane, who obtained 80 wt% of insoluble fraction. In our previous work, a similar system based on furfuryl mercaptan was studied [66]. The obtained results showed an insoluble fraction of 79% for a crosslinking density of 1.7 mol·m^{-3}. We can deduce that the new thioalkoxysilane-based system displayed better results than the systems based on the thiol–ene and Diels–Alder reactions. However, if the 3-MTS HC sample presents better results than the other systems, this observation can be attributed to the different percentages introduced in the formulations (27 wt% of 3-MTS, 0.5–1.0 wt% for the DCP system and 6 wt% for the furfuryl mercaptan system).

The 3-MTS HC sample was analyzed by rheological measurement in order to compare the variation of the elastic modulus between 100 and 0.01 rad·s^{-1} at 160°C with the DCP-crosslinked system (Fig. 13).

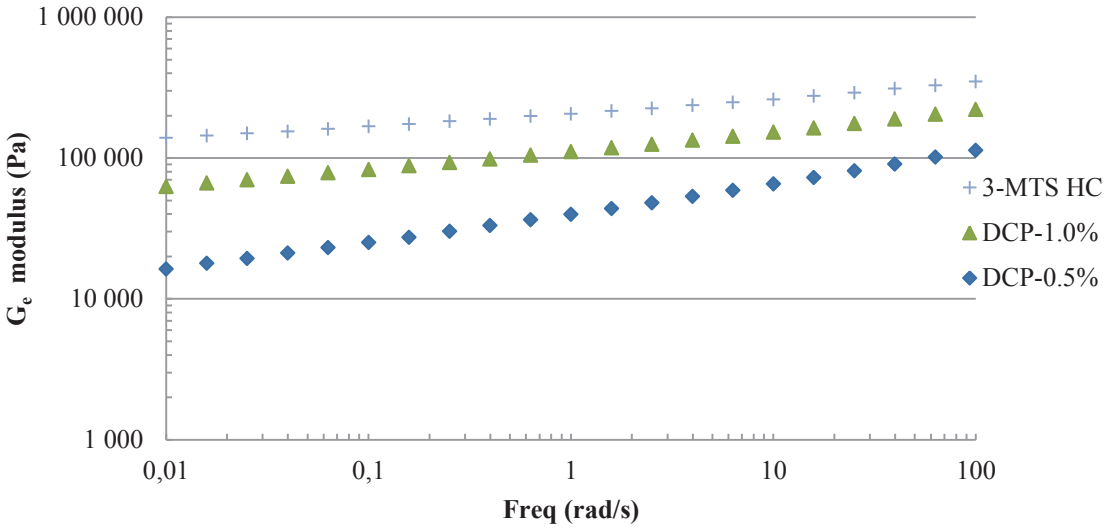


Fig. 13. Variation of the elastic modulus G_e versus freq (rad/s) at 160°C for EPDM samples formulated with 3-MTS, 1.0%wt of DCP and 0.5%wt of DCP.

First, the analysis of the curves reveals a difference in the rheological behavior for the two concentrations of DCP. At 0.01 rad·s^{-1} the difference between the equilibrium shear moduli is more pronounced: the G_e is 1×10^4 Pa for the sample containing 0.5 wt% of DCP and 6×10^4 Pa for 1.0 wt% of DCP. The increase of the modulus at low frequency is in agreement with the increase of the crosslinking density, corresponding to the increase of the DCP concentration. In comparison, the 3-MTS HC sample has a modulus value of 10^5 Pa at 0.01 rad·s^{-1}, which is higher than that of the DCP-1.0% sample. These rheological analyses confirm that the thioalkoxysilane-based systems allow us to obtain a superior elastic modulus than for the DCP-based systems.

- ***Mechanical properties***

Table 3 shows the results of the compression set obtained with the same samples compressed by 25% at 100°C for 24 h.

Table 3. Compression set and tensile test results for different EPDM formulation with thiol-alkoxysilane and DCP based systems

	DCP-0.5%	*DCP-1.0%*	*3-MTS HC*
DRC (%)	72±2	61±2	53±2
Max Stress (MPa)	0.7±0.1	2.6±0.3	2.2±0.10
Breaking strain (%)	****	2500±90	1440±50
Modulus of Elasticity (MPa)	0.4±0.1	0.4±0.1	1.2±0.1

We can observe that the 3-MTS HC sample has a recovery after 30 min of 53%, slightly superior to the value obtained with 1.0 wt% of DCP (61%). For the formulation with 0.5 wt% of DCP, the value is higher, with a value of 72%. These results correspond to a formulation composed of resol with a range between 10 and 30 phr [68] and confirm again the better efficiency of thioalkoxysilane systems compared with the DCP-based systems.

The final mechanical analysis conducted on the crosslinking sample is the tensile test, which allow us to determine the Young's modulus, the elongation at break and the maximum stress characteristics. Results and curves are depicted in Table 3 and Fig. 14 respectively.

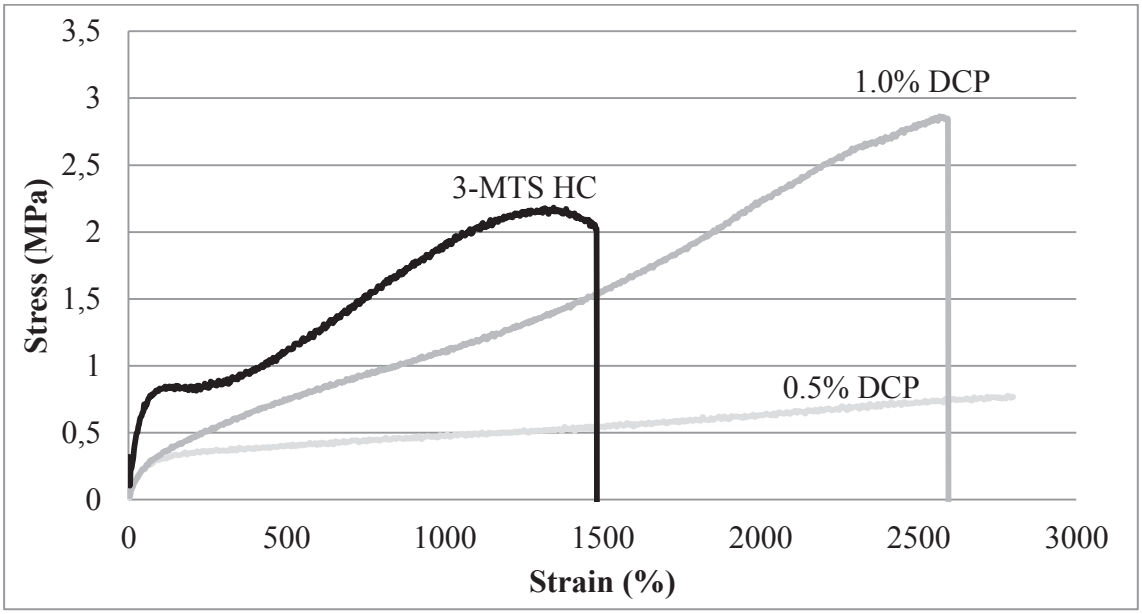


Fig. 14. Tensile curve stress versus strain at room temperature for a traction speed of 500mm/min

These results show different mechanical behaviors between the thioalkoxysilane and DCP-based systems. The modulus of elasticity increases, with a value of 1.2 MPa for 3-MTS HC versus 0.40 MPa for the DCP-based formulation. The maximum stress and the breaking

strain are relatively similar compared with the DCP-based system, with a value of 2.2 MPa of the maximum stress for the 3-MTS HC and 2.6 MPa for 1.0 wt% of DCP. Concerning the breaking strain, the values are over 2700% for 0.5 wt% of DCP and around 2500% for 1.0 wt% of DCP, in comparison with the value of around 1440% for the 3-MTS HC system.

- ***Morphology analysis***

The morphology of the 3-MTS HC sample is shown in **Erreur ! Source du renvoi introuvable.**. On these pictures, we can see the presence of spherical particles of a silica-like network due to the incompatible nature of the two phases, as widely observed in previous work [69-72]. **Erreur ! Source du renvoi introuvable.** shows the presence of some larger aggregates (around 25–30 μm). However, we notice a broad distribution of spherical particles, from 500 nm to 10 μm, which shows relatively large size dispersity.

IV- Conclusion

In this study, we have developed a novel alternative method for crosslinking an EPDM matrix with a reactive vegetable oil, tung oil, and a reactive agent, 3-MTS. We combined the thiol–ene and the alkoxysilane hydrolysis–condensation reactions to graft the reagent onto the EPDM matrix and react it with the tung oil double bonds. This approach allows us to improve the mechanical and chemical properties compared with other thiol systems. In this work, we also compared this crosslinking system with two sample references (0.5 and 1.0 wt% of DCP, with 30 wt% of mineral plasticizer), and the results showed a higher crosslinking density compared with the peroxide-based system. The compression set and rheological analysis showed superior results to those obtained with 1.0 wt% of DCP. These results are very encouraging for the development of alternative crosslinking reactions based on reactive vegetable oils and di-functional agents. We demonstrated that our system is able to create a dense crosslinking network, presenting good mechanical and chemical properties.

Acknowledgments: We thank NOVANCE and ACTIVATION for providing the neat and the modified oils, and HUTCHINSON companies for their work on EPDM polymers. We also thank EVEA for life cycle analysis of different oils, the poles of competitiveness TECHTERA, ELASTOPOLE and IAR for their support and finally the HUMEVERE project.

V- References

1. Cartasegna, S., *Silane-grafted moisture-curable ethylene-propylene elastomers for the cable industry.* Rubber Chemistry and Technology, 1986. **59**(5): p. 722-739.
2. Shieh, Y.T. and C.M. Liu, *Silane crafting reactions of LDPE, HDPE, and LLDPE.* Journal of Applied Polymer Science, 1999. **74**(14): p. 3404-3411.
3. Shieh, Y.T., J.S. Liau, and T.K. Chen, *An investigation of water crosslinking reactions of silane-grafted LDPE.* Journal of Applied Polymer Science, 2001. **81**(1): p. 186-196.
4. Narkis, M., et al., *Some properties of silane-grafted moisture-crosslinked polyethylene.* Polymer Engineering and Science, 1985. **25**(13): p. 857-862.
5. Sen, A.K., et al., *Kinetics of silane grafting and moisture cross-linking of polyethylene and ethylene propylene rubber.* Journal of Applied Polymer Science, 1992. **44**(7): p. 1153-1164.
6. Parent, J.S., et al., *Silane-modified poly(ethylene-co-vinyl acetate): Influence of comonomers on peroxide-initiated vinylsilane crafting.* Journal of Applied Polymer Science, 2000. **76**(8): p. 1308-1314.
7. Palmlof, M. and T. Hjertberg, *Catalysis of the crosslinking reactions of ethylene vinyl silane copolymers using carboxylic acids and DBTDL.* Journal of Applied Polymer Science, 1999. **72**(4): p. 521-528.
8. Shieh, Y.T. and K.I. Hsiao, *Thermal properties of silane-grafted water-crosslinked polyethylene.* Journal of Applied Polymer Science, 1998. **70**(6): p. 1075-1082.
9. Shieh, Y.T., J.S. Chen, and C.C. Lin, *Thermal fractionation and crystallization enhancement of silane-grafted water-crosslinked low-density polyethylene.* Journal of Applied Polymer Science, 2001. **81**(3): p. 591-599.
10. Shieh, Y.T. and H.C. Chuang, *DSC and DMA studies on silane-grafted and water-crosslinked LDPE/LLDPE blends.* Journal of Applied Polymer Science, 2001. **81**(7): p. 1808-1816.
11. Celina, M. and G.A. George, *Characterization and degradation studies of peroxide and silane cross-linked polyethylene.* Polymer Degradation and Stability, 1995. **48**(2): p. 297-312.
12. Shah, G.B., M. Fuzail, and J. Anwar, *Aspects of the crosslinking of polyethylene with vinyl silane.* Journal of Applied Polymer Science, 2004. **92**(6): p. 3796-3803.
13. Sirisinha, K. and S. Chimdist, *Comparison of techniques for determining crosslinking in silane-water crosslinked materials.* Polymer Testing, 2006. **25**(4): p. 518-526.
14. Sirisinha, K. and D. Meksawat, *Changes in properties of silane-water crosslinked metallocene ethylene-octene copolymer after prolonged crosslinking time.* Journal of Applied Polymer Science, 2004. **93**(2): p. 901-906.
15. Sirisinha, K. and D. Meksawat, *Comparison in processability and mechanical and thermal properties of ethylene-octene copolymer crosslinked by different techniques.* Journal of Applied Polymer Science, 2004. **93**(3): p. 1179-1185.
16. Zhang, G.Q., et al., *Performance evaluation of silane crosslinking of metallocene-based polyethylene-octene elastomer.* Journal of Applied Polymer Science, 2006. **102**(5): p. 5057-5061.
17. Jiao, C.M., et al., *Silane grafting and crosslinking of ethylene-octene copolymer.* European Polymer Journal, 2005. **41**(6): p. 1204-1211.
18. Hjertberg, T., M. Palmlof, and B.A. Sultan, *Chemical-reactions in cross-linking of copolymers of ethylene and vinyltrimethoxy silane.* Journal of Applied Polymer Science, 1991. **42**(5): p. 1185-1192.

19. Sirisinha, K. and K. Kawko, *Crosslinkable polypropylene composites made by the introduction of silane moieties.* Journal of Applied Polymer Science, 2005. **97**(4): p. 1476-1483.
20. Wang, Z.Z., et al., *Thermal and crystallization behavior of silane-crosslinked polypropylene.* Polymer International, 2005. **54**(2): p. 442-447.
21. Beltran, M. and C. Mijangos, *Silane grafting and moisture crosslinking of polypropylene.* Polymer Engineering and Science, 2000. **40**(7): p. 1534-1541.
22. Sirisinha, K. and K. Kawko, *Properties and characterization of filled poly(propylene) composites crosslinked through siloxane linkage.* Macromolecular Materials and Engineering, 2005. **290**(2): p. 128-135.
23. Fernandez, O.S.R. and M. Gilbert, *Properties of aminosilane grafted moisture curable poly(vinyl chloride) formulations.* Polymer Engineering and Science, 1999. **39**(7): p. 1199-1206.
24. RodriguezFernandez, O.S. and M. Gilbert, *Aminosilane grafting of plasticized poly(vinyl chloride) .2. Grafting and crosslinking reactions.* Journal of Applied Polymer Science, 1997. **66**(11): p. 2121-2128.
25. Anderlik, R. and H.G. Fritz, *Preparation of thermoplastic elastomers by dynamic cross-linking of silane-grafted ep-rubber.* Kautschuk Gummi Kunststoffe, 1992. **45**(7): p. 527-530.
26. Sen, A.K., et al., *Kinetics of silane grafting and moisture crosslinking of polyethylene and ethylene propylene rubber.* Journal of Applied Polymer Science, 1992. **44**(7): p. 1153-1164.
27. Ranney, M. and C. Pagano, *Silane coupling agent effects in ethylene propylene diene terpolymers.* Rubber Chemistry and Technology, 1971. **44**(4): p. 1080-1092.
28. Mittal, K.L., *Silanes and other coupling agents*. Vol. 4. 2007: CRC Press.
29. Sirisinha, K. and D. Meksawat, *Changes in properties of silane–water crosslinked metallocene ethylene-octene copolymer after prolonged crosslinking time.* Journal of Applied Polymer Science, 2004. **93**(2): p. 901-906.
30. Kim, J.-T., et al., *Characteristics of nitrile–butadiene rubber layered silicate nanocomposites with silane coupling agent.* Journal of Applied Polymer Science, 2003. **89**(10): p. 2633-2640.
31. Park, S.J. and K.S. Cho, *Filler-elastomer interactions: influence of silane coupling agent on crosslink density and thermal stability of silica/rubber composites.* Journal of Colloid and Interface Science, 2003. **267**(1): p. 86-91.
32. Luginsland, H.D., J. Frohlich, and A. Wehmeier, *Influence of different silanes on the reinforcement of silica-filled rubber compounds.* Rubber Chemistry and Technology, 2002. **75**(4): p. 563-579.
33. Nakamura, Y., et al., *Mechanical Properties of Silane-Treated, Silica-Particle-Filled Polyisoprene Rubber Composites: Effects of the Loading Amount and Alkoxy Group Numbers of a Silane Coupling Agent Containing Mercapto Groups.* Journal of Applied Polymer Science, 2009. **113**(3): p. 1507-1514.
34. Kaewsakul, W., et al., *Mechanistic Aspects of Silane Coupling Agents With Different Functionalities on Reinforcement of Silica-Filled Natural Rubber Compounds.* Polymer Engineering and Science, 2015. **55**(4): p. 836-842.
35. Fukuda, T., et al., *Mechanical properties of silica particle-filled styrene-butadiene rubber composites containing polysulfide-type silane coupling agents: Influence of loading method of silane.* Journal of Applied Polymer Science, 2013. **130**(1): p. 322-329.
36. Noriman, N.Z. and H. Ismail, *Properties of styrene butadiene rubber (SBR)/recycled acrylonitrile butadiene rubber (NBRr) blends: The effects of carbon black/silica*

(CB/Sil) hybrid filler and silane coupling agent, Si69. Journal of Applied Polymer Science, 2012. **124**(1): p. 19-27.
37. Gonzalez, L., et al., *Applications of an azide sulfonyl silane as elastomer crosslinking and coupling agent.* Journal of Applied Polymer Science, 1997. **63**(10): p. 1353-1359.
38. Liu, N.C., G.P. Yao, and H. Huang, *Influences of grafting formulations and processing conditions on properties of silane grafted moisture crosslinked polypropylenes.* Polymer, 2000. **41**(12): p. 4537-4542.
39. Lai, S.M., et al., *Fracture behaviors of PP/mPE thermoplastic vulcanizates via silane crosslinking.* Journal of Polymer Engineering, 2008. **28**(4): p. 203-223.
40. Fu, C., et al., *Properties of alkoxysilane castor oil synthesized via thiol-ene and its polyurethane/siloxane hybrid coating films.* Progress in Organic Coatings, 2014. **77**(8): p. 1241-1248.
41. Bétron, C., et al., *Diffusion of modified vegetables oils in thermoplastic polymers.* submit, 2016.
42. Sato, T., et al., *Comparison of Hansen Solubility Parameter of Asphaltenes Extracted from Bitumen Produced in Different Geographical Regions.* Energy & Fuels, 2014. **28**(2): p. 891-897.
43. Bétron, C., V. Bounor-Legaré, and P. Cassagnau, *Control of diffusion and exudation of vegetable oils in EPDM copolymers.* European polymer Journal submit, 2016: p. 26.
44. Neuburger, N.A. and B.E. Eichinger, *Critical experimental test of the Flory-Rehner theory of swelling.* Macromolecules, 1988. **21**(10): p. 3060-3070.
45. Chi, M.S., *Compatibility of cross-linked polymers with plasticizers by glass-transition temperature-measurement and swelling tests.* J. Polym. Sci. Part A: Polym. Chem, 1981. **19**(7): p. 1767-1779.
46. Flory, P.J., *Statistical mechanics of swelling of network structures.* Journal of Chemical Physics, 1950. **18**(1): p. 108-111.
47. Flory, P.J. and J. Rehner, *Statistical Mechanics of Cross-Linked Polymer Networks II. Swelling.* The Journal of Chemical Physics, 1943. **11**(11): p. 521-526.
48. Patel, S.K., et al., *Elastic modulus and equilibrium swelling of poly(dimethylsiloxane) networks.* Macromolecules, 1992. **25**(20): p. 5241-5251.
49. Sheehan, C.J. and A.L. Bisio, *Polymer/Solvent Interaction Parameters.* Rubber Chemistry and Technology, 1966. **39**(1): p. 149-192.
50. Peng, Z., et al., *Reinforcement of EPDM by in situ prepared zinc dimethacrylate.* Journal of Applied Polymer Science, 2002. **84**(7): p. 1339-1345.
51. Jose T, S. and J. Rani, *EPDM/CIIR Blends: Effect of EPDM Grade on Mechanical Properties.* International Journal of Polymeric Materials and Polymeric Biomaterials, 2007. **56**(7): p. 743-758.
52. El-Sabbagh, S.H., A.I. Hussain, and M.A.A. El-Ghaffar, *Utilisation of maleic anhydride and epoxidised soyabean oil as compatibilisers for NBR/EPDM blends reinforced with modified and unmodified polypropylene fibres.* Pigment & Resin Technology, 2005. **34**(4): p. 203-217.
53. Hrnjak-Murgić, Z., J. Jelenčić, and M. Bravar, *The role of molar volume of the organic solvents in the swelling system EPDM vulcanizate/solvent.* Die Angewandte Makromolekulare Chemie, 1996. **242**(1): p. 85-96.
54. Chen, J., et al., *Synthesis and application of a natural plasticizer based on cardanol for poly(vinyl chloride).* Journal of Applied Polymer Science, 2015. **132**(35): p. n/a-n/a.

55. Altenhofen da Silva, M., et al., *Polyvinylchloride (PVC) and natural rubber films plasticized with a natural polymeric plasticizer obtained through polyesterification of rice fatty acid.* Polymer Testing, 2011. **30**(5): p. 478-484.
56. *ASTM Standards, Designation D 395 (ISO 815) Standard Test Methods for Rubber Property-Compression Set*, 1989. p. 34-38.
57. Joubert, C., et al., *Influence of the crosslink network structure on stress-relaxation behavior: Viscoelastic modeling of the compression set experiment.* J. Polym. Sci. Part B: Polym. Physi, 2003. **41**(15): p. 1779-1790.
58. Posner, T., *Beiträge zur Kenntniss der ungesättigten Verbindungen. II. Ueber die Addition von Mercaptanen an ungesättigte Kohlenwasserstoffe.* Berichte der deutschen chemischen Gesellschaft, 1905. **38**(1): p. 646-657.
59. Silveira, C.C., S.R. Mendes, and F.M. Líbero, *Solvent-Free Anti-MarkovnikovAddition of Thiols to Alkenes Using Anhydrous Cerium (III) Chloride as Catalyst.* Synlett, 2010. **2010**(05): p. 790-792.
60. Wu, J.F., et al., *Synthesis of Soybean Oil-Based Thiol Oligomers.* ChemSusChem, 2011. **4**(8): p. 1135-1142.
61. Tyson, E.L., M.S. Ament, and T.P. Yoon, *Transition Metal Photoredox Catalysis of Radical Thiol-Ene Reactions.* Journal of Organic Chemistry, 2013. **78**(5): p. 2046-2050.
62. Hoyle, C.E. and C.N. Bowman, *Thiol-Ene Click Chemistry.* Angewandte Chemie-International Edition, 2010. **49**(9): p. 1540-1573.
63. Shostakovskii, M.F., E. Gracheva, and N. Kul'bovskaya, *Methods of preparation and properties of substituted vinyl ethers and sulphides.* Russian Chemical Reviews, 1961. **30**(4): p. 207-219.
64. Cao, C., L.R. Fraser, and J.A. Love, *Rhodium-catalyzed alkyne hydrothiolation with aromatic and aliphatic thiols.* Journal of the American Chemical Society, 2005. **127**(50): p. 17614-17615.
65. Hoyle, C.E., T.Y. Lee, and T. Roper, *Thiol–enes: Chemistry of the past with promise for the future.* J. Polym. Sci. Part A: Polym. Chem, 2004. **42**(21): p. 5301-5338.
66. Bétron, C., P. Cassagnau, and V. Bounor-Legare, *EPDM crosslinking from bio-based vegetable oil and Diels-Alder reactions.* journal of polymer science part A: Polymer Chemistry submit, 2016.
67. Brochier Salon, M.-C., et al., *Kinetics of hydrolysis and self condensation reactions of silanes by NMR spectroscopy.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2008. **312**(2–3): p. 83-91.
68. Martin, G., et al., *Viscoelasticity of randomly crosslinked EPDM networks.* Polymer, 2008. **49**(7): p. 1892-1901.
69. Carlberg, M., D. Colombini, and F.H.J. Maurer, *Ethylene-propylene-rubber (EPR)/polydimethylsiloxane (PDMS) binary polymer blends: Morphology and viscoelastic properties.* Journal of Applied Polymer Science, 2004. **94**(5): p. 2240-2249.
70. Acharya, H. and S.K. Srivastava, *EPDM/Silicone Blend Layered Silicate Nanocomposite by Solution Intercalation Method: Morphology and Properties.* Polymer Composites, 2014. **35**(9): p. 1834-1841.
71. Kole, S., et al., *Influence of curative, filler, compatibilizer, domain size, and blend ratio on the dynamic mechanical-properties of silicone epdm blends.* Journal of Applied Polymer Science, 1993. **48**(3): p. 529-545.
72. Kole, S. and D.K. Tripathy, *Morphology and aging behavior of silicone-epdm blends.* Journal of Materials Science, 1994. **29**(9): p. 2431-2435.

Conclusions et perspectives

Ces travaux de recherche ont été réalisés dans le cadre du projet HUMEVERE afin de mettre en place une solution de remplacement des plastifiants issus des ressources fossiles par des plastifiants issus de l'agro-ressource. Au cours de cette thèse, nous avons développé différentes méthodes de plastifications et de réticulations d'une matrice élastomère apolaire par des huiles végétales naturellement polaires qui sont donc peu compatibles. Le but de ces travaux a donc été d'intégrer ces huiles végétales dans la matrice tout en limitant le nombre d'étapes de synthèses, l'utilisation de solvant et de catalyseur afin de garder un procédé écologiquement viable. Les résultats peuvent être résumés principalement comme suit :

I- Mécanisme de diffusion et plastification par des huiles végétales

Dans cette partie, nous avons utilisé comme outil de prédiction le calcul des paramètres de solubilité de Hansen. Cet outil mathématique a été confronté à des expériences de diffusions par rhéologie afin de déterminer la fiabilité de ce dernier en conditions réelles. Les résultats ont mis en évidence que si cette théorie était capable de discriminer des molécules avec des fonctions incompatibles, et donc d'éliminer facilement les plus mauvais candidats, il a été beaucoup plus difficile de réellement prédire la solubilité d'un plastifiant vis-à-vis d'une matrice. En effet, les mécanismes de diffusion sont complexes et mettent en jeu divers paramètres comme la masse molaire, la géométrie moléculaire, l'énergie d'activation, etc.. Qui sont autant de paramètres difficilement modélisables mathématiquement sans des calculs complexes et qui donc rendent l'expérimentation nécessaire en raison de sa facilité de mise en œuvre et sa fiabilité par rapport à des modèles théoriques plus complexes.

Ce travail préliminaire a donc permis de comprendre les mécanismes et les fonctions chimiques favorables à la plastification de matrices polymère par des huiles et de sélectionner un certain nombre de candidats bio-sourcés comme agent de substitution des plastifiants actuels. Malheureusement, la plastification de la matrice élastomère par des huiles végétales a soulevé plusieurs problèmes. Tout d'abord les huiles végétales ont naturellement une affinité limitée avec la matrice EPDM du fait de la présence de triesters. Outre la difficulté d'incorporation de certaines huiles, les tests d'exsudations effectués après incorporation de 30% en masse dans la matrice EPDM ont mis en évidence des pertes de matières importantes. Cette exsudation entraine une diminution des propriétés mécaniques du matériau au cours du temps et rend donc ce dernier non viable. Nous avons donc utilisé des huiles végétales modifiées possédant une meilleure diffusion et une compatibilité légèrement améliorée avec la matrice. Néanmoins malgré une meilleure diffusion, la problématique d'exsudation reste entière.

Il est donc apparu que la modification des huiles végétales en amont permettant de les rendre compatibles n'était pas une solution viable. Nous avons par la suite travaillé sur un moyen de figer l'huile végétale une fois incorporée dans la matrice élastomère. Pour ce faire, nous avons utilisé la réaction de standolie consistant à faire homopolymériser une huile végétale sur elle-même par traitement thermique. Cette réaction est réalisée en absence d'oxygène pour éviter le phénomène d'oxydation, et la création de ponts oxygènes qui ne sont pas compatibles avec la matrice EPDM. Pour ce faire, nous avons utilisé l'huile de Tung ayant la particularité d'être assez réactive pour pouvoir effectuer cette réaction à une température compatible avec la mise en œuvre de la matrice. La réaction a été suivie avec

succès par rhéologie dans un premier temps avec juste de l'huile de Tung, puis dans un second temps dans un mélangeur interne après incorporation de l'huile végétale. Les résultats obtenus ont démontré que l'huile de Tung a été capable de réagir sur elle-même sans réticuler la matrice polymère. Enfin, le matériau obtenu avec cette méthode ne présentait plus de signes d'exsudations, confirmant l'efficacité du procédé.

II- Réticulation de la matrice élastomère avec l'huile de Tung

Fort des résultats obtenus lors de la plastification de l'EPDM par l'huile de Tung, nous avons envisagé dans un second temps d'ajouter une propriété de réticulation supplémentaire à notre procédé à base d'huile agrosourcée.

Dans ce contexte, nous avons décidé non plus de faire réagir l'huile uniquement sur elle-même, mais de la faire réagir également avec la matrice EPDM. Malheureusement, les fonctions réactives présentent sur la matrice EPDM étant limitées, les chimies pouvant répondre au cahier des charges imposant une chimie écoresponsable le sont aussi. Nous avons donc décidé d'utiliser deux réactions. La réaction Thiol-ène permet une réaction sur les insaturations de la matrice et l'huile de Tung et a pour avantage de pouvoir être mise en place dans des conditions relativement douces (élévation de température, sans solvant ni catalyseur). Par ailleurs, la réaction de Diels-Alder, possède également l'avantage de pouvoir être mise en place à plus haute température. Nous avons donc sélectionné un « comptabilisant » possédant ces deux fonctionnalités, le 2-furanmethanethiol, ce produit ayant la particularité d'être utilisé dans l'agroalimentaire et donc d'être inoffensif *(à faible dose)*.

Nous avons donc développé avec l'utilisation de cet agent un procédé continu en 3 étapes, sans utilisation de solvant, ni de catalyseur et permettant de lier l'huile de Tung et la matrice EPDM entre eux avec la formation d'un réseau uniquement par traitement thermique. Nous avons comparé le matériau obtenu avec un échantillon de référence d'EPDM plastifié avec de l'huile minérale et réticulé avec du DCP. Nous avons déterminé que les propriétés mécaniques (DRC et rhéologique) et chimiques (densité de réticulation et gonflement) pouvaient être apparentées à une réticulation avec 1% en masse de DCP. Néanmoins, les tests mécaniques de traction ont mis également en lumière une résistance moindre de notre échantillon bio-basé par rapport à l'échantillon de référence en termes d'élongation et de résistance à la rupture.

Enfin, dans un second temps nous avons également développé un autre procédé de réticulation basé sur des réactions d'hydrolyse-condensation de silane couplé avec une fonctionnalité thiol. Pour ce faire, nous avons utilisé comme « comptabilisant » le 3-mercaptopropyltrimethoxysilane. La mise en place de ce système a nécessité des étapes supplémentaires d'hydrolyse et de condensation par rapport au système précédent ce qui le rend un peu plus délicat à mettre en place industriellement. Néanmoins, les résultats obtenus ont mis en évidence des caractéristiques mécaniques et chimiques similaires voir supérieurs dans certain domaine au système de référence et également au système développé précédemment.

III-Perspectives

Lors de cette étude, nous avons constaté que la transition vers des ressources renouvelables ne peut avoir lieu sans le développement de procédés spécifiques du fait de l'incompatibilité native des huiles végétales avec des matrices apolaires.

Si les méthodes que nous avons utilisées nous ont permis d'obtenir des résultats encourageants et donc de mettre en lumière la faisabilité de ce procédé, il subsiste néanmoins un certain nombre de problèmes et d'études à réaliser pour améliorer et mieux comprendre les mécanismes mis en jeux.

En effet, il serait intéressant de pousser plus loin les analyses chimiques des systèmes réticulants pour obtenir un suivi direct des réactions en fonction de la température, par exemple par IR, et cela pour bien comprendre la mise en place du réseau de réticulation afin de mieux le contrôler.

Un autre problème inhérent à l'utilisation de la chimie du soufre concerne les fonctions thiol résiduelles. Ces fonctions particulièrement odorantes posent un problème pour l'utilisation des matériaux obtenus. Il est donc obligatoire de traiter les échantillons obtenus pour neutraliser les fonctions thiol restantes, par exemple par oxydation avec du peroxyde d'hydrogène en fin de procédé.

Concernant la réticulation par réaction d'hydrolyse-condensation des fonctions alkoxysilane, l'étape induite rend le procédé plus compliqué à mettre en place à l'échelle industrielle. Néanmoins, il serait judicieux d'envisager cette réaction lors d'un procédé continu, par exemple en extrusion en injectant tout simplement de l'eau acide.

On peut également se poser la question de la tenue dans le temps face aux agressions environnementales de tel système composé majoritairement de produit issu de l'agroressource et donc particulièrement sensible aux UV et aux attaques biologiques (champignons, bactérie, etc…)

Enfin, pour des questions de facilité de compréhension, cette étude s'est concentrée sur un système modèle, composé uniquement d'une matrice EPDM, d'un plastifiant et d'un agent réticulant. Mais ce système ne représente pas la réalité d'une formulation industrielle et devrait être testé dans un système TPV afin de vérifier que les résultats obtenus sont transposables industriellement.

Comme nous venons de le voir, il reste donc un certain nombre de points à étudier pour comprendre tous les mécanismes mis en jeux lors de ces procédés de diffusion et de réticulation. Cette étude est une première approche dans le cadre d'une future transition vers des procédés et des formulations plus respectueuses de l'environnement, mais nécessite encore des travaux d'approfondissement et de compréhensions pour avoir une réalité industrielle.

Développement et fonctionnalisation d'huiles végétales pour la plastification et la réticulation d'élastomères

L'objectif de ces travaux de thèse consiste à étudier la faisabilité du remplacement des huiles issues des ressources fossiles par des huiles végétales dans des matrices polymères.
La première partie étudie la diffusion des huiles dans les matrices EPDM et PVC, en confrontant le modèle théorique des paramètres de solubilités de Hansen à des tests de diffusions suivis par rhéologie. Les résultats ont été analysés afin de mettre en évidence les avantages et les faiblesses de ce type de modèle.
Dans un second temps, nous avons formulé une matrice élastomère en utilisant des plastifiants à base d'huiles végétales et vérifié avec différents tests l'efficacité de ces plastifiants. Les résultats ont mis en évidence des problèmes d'incompatibilité entre la matrice EPDM et les huiles agrosourcées. Une méthode de modification *in situ* a donc été utilisée sur de l'huile de Tung afin de fixer l'huile végétale dans la matrice.
Enfin dans une dernière partie nous avons apporté différentes propriétés de réticulations à l'huile de Tung. Nous avons développé deux systèmes de réticulations basés sur des molécules di-fonctionnelles, le 2-furanmethanethiol et le 3-mercaptopropyltriethoxysilane. Au cours d'un procédé continu de mélangeage, nous avons greffé le 2-furanmethanethiol sur la matrice et sur l'huile végétale grâce à une réaction thiol-ène et une réaction de Diels-Alder, ce qui nous a permis de réticuler le système. Nous avons également étudié une autre molécule capable de créer des nœuds siloxanes à partir de réactions d'hydrolyse-condensations de fonctions alkoxysilanes après greffage sur la matrice EPDM et sur l'huile par réaction thiol-ène. Les résultats obtenus ont montré des propriétés similaires à un système de réticulation classique avec du dicumyl peroxide (DCP).

Development and functionalization of vegetable oils for plastification and crosslinking of elastomers matrix

The aim of the thesis is to study the feasibility of replacing the fossil oils by vegetable oils in polymer matrices.
The first section discusses the diffusion of oil in EPDM and PVC matrices. This study was carried out by confronting the theoretical model of the Hansen solubility parameters to experiment rheology tests. The results were analyzed to highlight the strengths and weaknesses of this model.
In second part, we used an elastomer formulation based on vegetable oils plasticizers. The effectiveness of these plasticizers has been verified using different tests. The results showed the problems of incompatibility between the EPDM matrix and the bio-based oils. *In situ* modification method was therefore used on Tung oil to fix the vegetable oil into the matrix.
Finally, in a last part we studied different properties of the crosslinked material. We have developed two crosslinking systems based on di-functional molecules, the 2-furanmethanethiol and 3-mercaptopropyltriethoxysilane. In a continuous process of mixing, we grafted the 2-furanmethanethiol on the matrix and on the Tung oil by thiol-ene and Diels-Alder reaction for crosslink the system. The 3-mercaptopropyltriethoxysilane has been grafted on the EPDM matrix and the Tung oil by similar process. The crosslinking was carried out by creating siloxane bonds from hydrolysis-condensation reactions of alkoxysilanes functions. The results showed similar properties to conventional crosslinking system with dicumyl peroxide (DCP).